# A THEORETICAL AND PRACTICAL TREATISE

ON THE

# MANUFACTURE

OF

# SULPHURIC ACID AND ALKALI,

WITH THE

## COLLATERAL BRANCHES.



BY

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VOLUME III.

LONDON:

JOHN VAN VOORST, PATERNOSTER ROW.

MDCCCLXXX.

ALERE FLAMMAM.

PRINTED BY TAYLOR AND FRANCIS,
RED LION COURT, FLEET STREET.

# PREFACE.

In presenting this third and concluding volume of my Treatise to the public, I would first of all return thanks for the numerous expressions of appreciation, printed, written, and verbal, which I have received with respect to the first two volumes.

No one can be less blind than myself to the many shortcomings of my work; but those communications seem to prove that my hope of doing something useful in the cause of chemical industry has not been altogether unwarranted. It could hardly be expected that my aim, to give a complete record of the theoretical and practical part of my subject, should be absolutely attained. For one man, even aided by so many kind counsels as I have been, it is hardly possible to gain cognizance of every thing which has been done and is doing in hundreds of vitriol- and alkali-works in all civilized countries; but I have tried to approach to this as nearly as practicable; and if I may believe my critics, nothing of any importance has been omitted.

In this respect my book differs greatly, and designedly (whether to its advantage or not it is not for me to say), from some others

which have appeared almost simultaneously with the first two volumes of my Treatise. Those other books aim at nothing but giving an accurate description of the present style of making sulphuric acid and alkali in England; and they leave the chemistry of the subject almost totally aside. My Treatise differs from this in several respects. First, it gives a detailed chemical description of the raw materials, intermediate and final products, of the modes of testing and so forth, supplemented by numerous tables of solubilities, densities, &c.; and it also enters very fully into the theory of all the processes concerned, accurately citing all papers on the subject, so that the reader can go to these for further elucidation. I am quite aware that a treatment of this kind will appear lengthy and superfluous to some readers, who look into this book merely for "practical" hints. In this respect they will not, I trust, be disappointed either; but I make bold to say that they would do very well not to despise the scientific part, the purely chemical detail, of this work. After all, our subject belongs to the domain of *Chemistry*, and the times are far behind us when, in the manufacture of chemical products, the practical man with his rule of thumb could look down upon the chemist in the laboratory—who, in the former's idea, was at best only good for testing the materials, but whose interference with the works would invariably cause mischief. That this was true to some extent, and still is so, where the chemist attempts to transfer his ideas into practice in a crude state without sufficient practical experience, nobody can possibly deny. But does the "practical man" on his part make no mistakes? Have not untold sums been wasted in futile "inventions" and "improvements" merely because "practical" inventors lacked a scientific knowledge of their subject? Probably very much larger sums have been lost in this way than by the deficiency in practical experience of "theoretical" inventors, for the simple reason that the latter class of inventors generally have not so much means at command as the former.

It is a mere truism that theory and practice should always go hand in hand; but it must nevertheless be inculcated over and over again, as would appear from the fact that several costly books on, perhaps, the most important branch of chemical industry have just been published with next to no chemistry in them. And to what consequences does this neglect of a scientific treatment of practical subjects lead? The author may be pardoned for illustrating this from his personal experience. A little more than sixteen years ago he left his native country for Great Britain, because chemical industry was too little developed in Germany, and he might justly hope to learn a great deal and find much more scope for himself in that country which he is proud to have made his second home. More particularly the manufacture of sulphuric acid, soda ash, and bleaching-powder was at that time quite insignificant in Germany, and not very considerable in France, as compared with Great Britain; nor could the technical appliances, the yields, or even the purity of the products in the two former countries vie with those of the latter. How different matters are now is a matter of notoriety. The manufacture of chemicals has made enormous strides forward, both in quantity and in quality, in France, and even more so in Germany. Many of the chemicals of these countries outstrip those of English works in purity; and their plant and their processes are frequently superior to those used in the majority of English works. Everybody knows how this has come about. The foreign chemists and manufacturers have looked all round, not merely in their own countries, but wherever they could find improved methods and apparatus; and upon the practical knowledge thus gained they have brought to bear the scientific training they had received at their universities and polytechnic schools. Thus they have already, in many fields formerly remunerative to British manufacturers, distanced the latter, immensely aided though these be by their long occupation of the ground and by permanent natural advantages, such as cheapness of coal and freight, superior command of

capital, &c.; and this is likely to go on to an increasing extent, if many British chemical-manufacturers decline to profit from a scientific study of their respective branches. This is all the less excusable, as England from of old has been a stronghold of scientific chemistry, and can hold its own against the whole world in that respect.

A second difference of my Treatise from others recently published in England is that the experience of other countries is fully drawn upon. I must leave it to competent readers to say whether, even as far as English plant and processes are concerned, any thing of importance to be found in other treatises is not sufficiently described in this book. But the latter is alone in bringing before the English reader in full detail, illustrated by a large number of scale drawings, the modes of manufacture practised in Germany, Austria, France, and Belgium. Some of the English manufacturers have seen the splendid alkali-works existing in those countries; and to their judgment the author confidently appeals for the expedience of devoting so much space to the description of foreign plant and processes.

Perhaps more objections might be raised to the fact that a certain, although not an unduly large, part of this work is devoted to historical notes and to a description of processes which have either been abandoned long since or which have never become practical, and are not likely ever to be so. Nay, I have even attempted to be as complete and exhaustive as possible, mentioning, although briefly, every thing which has come under my notice in studying the literature and the patent-records of various countries. But I trust to be justified in this respect as well. Who is bold enough, in every instance, to decide whether a patent is quite useless and exploded? Do not many proposals which appear impracticable at first sight, or which have been tried and abandoned again, or which have never been tried at all, contain the germ of much that is extremely valuable? This is best proved

by the fact, abundantly illustrated in this book, that there is hardly a single great improvement in industrial chemistry which has not been preceded by many abortive attempts in the same (that is, in the right) direction—abortive merely because not enough patience, capital, knowledge, and practical ingenuity were expended on them. Hence in the ever continuing and ever increasing stream of inventions, a complete record of all that has previously been done, or merely proposed to be done, should be welcome to the would-be inventor. It will guide him, both by suggesting to him ideas and encouraging him to follow up the lines first traced by others in the past, and not less by informing him of the failure of some ideas which he may have conceived for himself without knowing that others had tried them already.

How many patents have been taken out in succession for substantially or completely the same thing! the money and loss of time for which would have been saved if the inventor could have first consulted a treatise like this, which gives to him (as far as the author has been able to do) a succinct report of all that has been done in his branch before, whether patented or not. Moreover, in all cases where it was possible, it is distinctly stated if, and why, a certain process had failed. It is evident that the most laborious study of the English patent-records by itself, infinitely more time though it would take, still would not yield any thing like the same results. No further apology seems needed for this feature of my book.

Particular attention must be directed to the voluminous Appendix, containing:—first, every thing published since the book has been in the printer's hands, down to the time when the sheets were revised; secondly, a large number of very important communications received by the author in the meanwhile. The bulk of these addenda naturally refer to the first volume—that is, to the manufacture of sulphuric acid; and they form an indispensable supplement to that volume. But a number

of important additions had also to be made to Vol. II., and a few even to Vol. III. For this last volume I have had the valuable privilege of obtaining Mr. Walter Weldon's friendly advice touching the Chapter treating of his chlorine-process; and I cannot but publicly thank him for his assistance, rendered in spite of bad health and urgent press of business occupations.

The Polytechnicum, Zurich,
October 1880.

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# CHAPTER XVI.

## THE AMMONIACAL SODA-PROCESS.

THE only process which has hitherto been capable of competing seriously with that of Leblanc is founded upon the conversion of ammonium carbonate and common salt into sodium bicarbonate and ammonium chloride, according to the equation

$$NaCl + (NH_4)HCO_3 = NH_4Cl + NaHCO_3.$$

The two latter salts can be easily separated, owing to the fact that sodium bicarbonate is very little soluble in a solution of sal-ammoniac and is separated in a crystallized form. Of course the ammonium carbonate must always be regenerated.

The principles of this process are clearly laid down in the patent of H. G. Dyar and J. Hemming, dated June 30, 1838. This invention, consequently, is undoubtedly an English one, though it only found its practical application on the continent. Dyar and Hemming mixed a saturated solution of common salt with an amount of powdered commercial ammonium carbonate equal in weight to the salt. The latter being only sesquicarbonate (mixed with ammonium carbonate), they remark that bicarbonate would be preferable. The decomposition takes place according to the above equation; and the solution formed is separated from the precipitated salt. The latter is chiefly sodium bicarbonate, mixed with a little ammonium carbonate, which is driven off by heating to 375° C., along with any ammonium chloride present and half the $CO_2$ of the $NaHCO_3$; all this is condensed in a lead chamber; and very pure soda remains behind. On the other hand, the solu-

tion contains chiefly ammonium chloride with a little sodium carbonate, sodium chloride, and ammonium carbonate. The latter is expelled by boiling and condensed in the lead chamber; the solution is boiled down to dryness, and the residue heated with calcium carbonate, whereby the ammonium chloride is transformed into carbonate, which is conveyed into the same lead chamber. The contents of the latter are used over again for converting common salt into soda; so that nothing but limestone is used up.

Dyar and Hemming's process was carried out by an English company at a place in Cheshire, and made also a great stir in Germany and Austria. Soon after 1840, Kunheim at Berlin and Seybel at Liesing near Vienna tried it; but the fact, published by Anthon in 1840, that a great deal of salt is left undecomposed, discouraged the manufacturers; and altogether the matter was not ripe yet. Other factories upon this system were erected by Deacon and Gossage at Widnes (in 1855), by Bowker in Leeds, by Muspratt at Newton Heath, another in 1842 at Vilvorde near Brussels, later on one by Turck at Sommervillers and by Schloesing and Rollond at Puteaux (see below).

We shall first enumerate the patents in their chronological order. H. Waterton (Aug. 27, 1840) decomposes common salt by sesqui- or bicarbonate of ammonium, already with the assistance of a current of carbonic acid. Chisholm (1852) makes soda and ammonium chloride from by-products of the purification of gas. He distils the $NH_4Cl$ with $CaCO_3$, and conducts the ammonium carbonate into a solution of common salt; or he distils $NH_4Cl$ with $CaO$, and then conducts the $NH_3$ along with $CO_2$ into the solution of $NaCl$. The French patents are those of Delaunay (May 27, 1839), Canning (1842), Grimes (1852). An English patent, again, is that of Gossage (Feb. 2, 1854). It contains nothing new in principle: but his apparatus (shown in fig. 1 in longitudinal section, and in fig. 2 at right angles to the axis) is interesting. It is a cylindrical vessel, divided into six chambers, $a_1$ to $a_6$, by partitions which do not quite join; it rests on the spindles *a* and *b*. *a* is solid, and is slowly turned round by the gearing *e* and *f* connecting it with the main shaft *g*; *b* is hollow, and runs into two glands *k k*, which leave between them a chamber into which two gas-pipes for $CO_2$ and $NH_3$ enter, which communicate with the hollow spindle by openings, allowing the gas to pass through; *d d* are openings closed by lids for introducing the

Fig. 1.

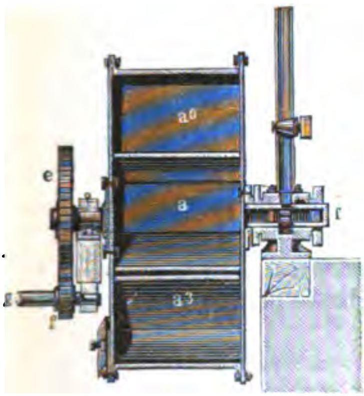



Fig. 2.


materials. The solution is run in above the axis; on the cylinder turning round it is scooped up by each chamber in turn, and is poured out again as each reaches the position of $a_1$. At the same time the gas rises through the liquid in bubbles; so that it is well mixed with and absorbed by the latter. At first the gases are introduced without pressure; at last the $CO_2$, in order to produce complete saturation, must be forced in with an excess pressure of at least 10 lb. to the square inch. Since in the condensation of gas much heat is given off, the solution must be cooled down at least to 37° C. before running it out. In the cylinder a solution of 1 part of salt in 3 parts of water is employed; the $CO_2$ is partly obtained by heating the sodium bicarbonate formed in the process in iron retorts. In place of the mixing-vessels described, a coke-tower can be employed, in which the gases ascend and the solution runs down. To the saturated solution of salt either so much solid ammonium sesqui- or bicarbonate is added that 17 parts of $NH_3$ are present for each 240 parts of brine, or into 240 parts of brine the $NH_3$ gas given off from 54 parts of $NH_4Cl$, and afterwards $CO_2$ under a pressure of 10 lb. per square inch, are passed. After the decomposition is finished, the mixture is filtered through canvas in a closed vessel; here the mass is first drained and the $NH_4Cl$ mixed with the $NaHCO_3$, then displaced by a solution of pure $NaHCO_3$.

The next patent is that of Turck in Nancy (1854); then that of Th. Schloesing (June 28, 1854). In horizontal cylinders, pro-

vided with an agitator, a solution of common salt is saturated with $CO_2$ and $NH_3$, and the unabsorbed $NH_3$ retained in coke-towers by a mixture of $CaCl_2$ and HCl; the $NaHCO_3$ was to be dried in a centrifugal machine, washed with a solution of pure sodium bicarbonate, and heated in a horizontal iron retort, in which an Archimedean screw slowly moved it along from the entrance end to the exit end. The escaping $CO_2$ was to be utilized for the next operation; and the $CO_2$ further required was to be furnished by a lime-kiln which at the same time heated the retort. With 100 parts of water 30 to 33 parts of common salt, $8\frac{1}{2}$ to 10 parts of $NH_3$ gas, and an excess of $CO_2$ were to be employed.

A few days after (July 8th, 1854), a communication from abroad was patented by Johnson, for obtaining pure carbonic acid from products of combustion, by absorbing them under pressure in a solution of sodium or potassium carbonate and driving it out again by heat (this process was once more patented ten years later by Ozouf, June 16th, 1864)—also for utilizing such pure $CO_2$ in the ammoniacal soda-manufacture; the escaping $NH_3$ was to be recovered in condensers similar to those employed for hydrochloric acid.

On Feb. 26th, 1855, Bellford patents a communication, the only "novelty" of which consists in obtaining from the impure bicarbonate pure soda by mixing it with water and submitting it to pressure, in case of need repeatedly; the solution was to be distilled, the ammonia condensed and submitted in a coke-tower to the action of carbonic acid from a lime-kiln.

On Aug. 30, 1855, Gossage patents the manufacture of ammonium bicarbonate by distilling the solution of sesqui- or monocarbonate, and the employment of the product of distillation, either in the state of vapour or after condensation, for decomposing common salt.

On Oct. 13, 1857, Bell patents the introduction of the gases from the dry distillation of leather or bones, after separating the tar, into solutions of salt for precipitating sodium bicarbonate. The novelty was to consist in the direct utilization of the distillation-gases; but this would hardly be practicable, on account of their impurities.

Schloesing and Rolland erected in 1855 an experimental factory at Puteaux, near Paris, for working Schloesing's patent of 1854.

This factory is said to have produced about 300 tons of soda in two years; but it was stopped in 1858, "owing to the bad state of trade and to the inconvenience caused by the monopoly of salt"*). On March 26th, 1858, they took out a new English patent, chiefly in order to make the process perfectly continuous. In the same apparatus, whilst a certain quantity of salt was converted into bicarbonate and removed from the vessel, a corresponding quantity of fresh NaCl was to be introduced, the corresponding quantity of $NH_3$ recovered from the filtered liquor and admitted into the brine; lastly, by calcining the bicarbonate and burning limestone the requisite quantity of $CO_2$ was to be obtained. They described their process at length in the Ann. Chim. Phys. [4] xiv. p. 5 (1868). Their apparatus consists of four or more horizontal cylinders, communicating with each other. Into one of these a solution of 30 parts NaCl in 100 water enters, circulates through all four cylinders, and runs out of the last one. To this solution 22 parts of ammonia, either in the gaseous state or dissolved in water, are admitted in the second cylinder. On travelling further the liquor is brought into contact first with lime-kiln gases, and at last with the $CO_2$ obtained by heating the bicarbonate and the liquid filtered from it. Within the cylinder there are a kind of paddle-wheels for distributing the liquid and facilitating the absorption; the cylinders are cooled on the outside by water. The gases are aspirated in the direction opposite to the flow of the liquid by a fan-blast, which at the same time causes a partial vacuum and prevents the escape of ammonia out of the joints. In order to retain the ammonia gas which escapes absorption (of which a portion remains already in the first cylinder, filled with pure NaCl solution), the exit gases are passed through a coke-tower fed with water; and this is afterwards employed for dissolving salt. From the last cylinder the solution of $NH_4Cl$ runs away along with the precipitated $NaHCO_3$; these are separated by a centrifugal machine and washed with a little water (in which $1\frac{3}{4}$ per cent. is lost by redissolving). The bicarbonate is dried and ignited in the above-mentioned cylindrical retort with Archimedean screw, and the $CO_2$ gas drawn off by an aspirator. The liquid separated from the bicarbonate is heated by steam to 60° or 70° C., to expel the $CO_2$, and then to 100° C. to expel the ammonia. It

* Solvay, in a pamphlet published for the Paris Exhibition of 1878, conclusively shows the utter insufficiency of this reason for discontinuing the process.

is next heated with milk of lime in a horizontal cylinder provided with an agitator; thus $NH_3$ is liberated, which is deprived of water by cooling and re-introduced into the converting-apparatus. From 167 parts NaCl 100 only $Na_2CO_3$ are obtained, instead of 151 indicated by theory, at a cost of 8·70 to 9·67 francs per 100 kilog. soda, according to the size of the works. [If the manufacturing process really had been so cheap, the works need not have stopped, in spite of the salt monopoly!] For making 100 kilog. of anhydrous soda the following quantities are stated to have been required:—

| kilog. | |
|---|---|
| 167·0 | NaCl = 180 kilog. crude salt or 5·57 hectolitres of saturated brine; |
| 68·5 | CaO = 122 kilog. limestone, = 135 kilog. with 10 per cent. moisture; |
| 32·0 | $NH_3$, of which at most 1 kilog. was lost; |
| 128·3 | coals for distilling and steam; |
| 72·0 | coke for the lime-kiln and for heating bicarbonate. |

In 1858 Heeren (Dingl. Journ. cxlix. p. 47) made an experimental research on the ammoniacal soda process. At the outset he makes the curious proposal to obtain pure $CO_2$ from limestone and muriatic acid; but where is the latter to come from, if the soda is to be made by the ammonia process? He further proposes purifying the brine from magnesia and lime by soda, filtering and saturating the clear liquor with $NH_3$ gas, viz. 44 parts $NH_3$ to 100 NaCl, by which only $\frac{2}{3}$ of the latter is decomposed; so that from 100 NaCl only 105, instead of 158, $NaHCO_3$ is formed. If only one equivalent of $NH_3$ to two NaCl is employed, the decomposition proceeds up to $\frac{4}{5}$ of the ammonia salt, the excess of salt being lost; but this is better than the opposite way, in which much $NH_3$ would be lost. Now $CO_2$ is passed into the liquid, which is very slowly absorbed unless assisted by pressure. The separation of the solution of $NH_4Cl$ from the precipitate of $NaHCO_3$ takes place as usual. The solution is distilled with lime, and the $NH_3$ condensed in brine, if fresh salt can be dissolved at the same time; if only brine is at disposal, the $NH_3$ gas must be deprived of water by cooling. If the ammonia is to be obtained as carbonate, the solution of $NH_4Cl$ is boiled down to dryness,

mixed with twice its weight of chalk and damp clay (the latter in order to remove the fused $CaCl_2$ more easily from the vessel), and heated to a low red heat in iron retorts. According to Heeren's calculation, 1 cwt. of this soda ash would cost 12*s*. 3*d*., without counting general expenses and muriatic acid; with these it would cost 16*s*. 6*d*. The bicarbonate would cost 14*s*. 6*d*. without, or 13*s*. per cwt. with HCl; this price is higher, because the manufacture must be carried on on a smaller scale.

The further development of the ammoniacal soda-process is intimately connected with the name of Ernest Solvay, of Couillet near Charleroi (Belgium). Undoubtedly Solvay was the first to carry out the process so as to make it a paying one, which none of his predecessors was able to do. But it is too much to identify the ammoniacal soda-process altogether with his name, as has been claimed for him. We have seen that very many had worked at the process before, and worked it out in all essential parts. What was wanting to make it an economical success was a practical combination of apparatus so as to avoid a great loss of ammonia. This Solvay has decidedly attained by his apparatus; but several others (for instance Honigmann, Gerstenhöfer) confidently assert the same thing of their apparatus. It cannot be said that the diploma of honour, conferred upon Solvay at the Vienna Exhibition of 1873, was not fully merited; but why was a similar diploma conferred upon Schloesing and Rolland, who had neither invented the process nor made it pay, whilst the real inventors, Dyar and Hemming, were entirely neglected?

Solvay's first patent (not an English one) dates from April 15th, 1861; his first English patent from September 12th, 1863, his second patent from May 18th, 1872, others from March 8th, May 5th and 20th, 1876, &c. The Couillet works were started in 1863; and soda made there was already exhibited in Paris in 1867, where it did not excite much attention; but his triumph was complete at the Vienna Exhibition of 1873. We will describe his process according to his (English and German) patent-specifications, guided by the inspection of the works of Messrs. Brunner, Mond, and Co. at Winnington Hall near Northwich, where Solvay's process has been introduced.

The salt employed is either natural brine or rock-salt. The former is greatly to be preferred, since the cost of evaporation or of winning the rock-salt, and that of dissolving are saved; the

salt in the brine at Dombasle, near Nancy, only costs about 1*s.*, at Northwich only 6*d.* per ton. Hitherto the ammonia process has only been successful where this condition is fulfilled. Still there are cases where fresh salt has to be dissolved for the purpose; and natural brine has frequently to be brought up by dissolving rock-salt in it. At Varangéville 1 ton of the latter is employed to 5 tons of salt in the brine. For *dissolving the salt,* Solvay has constructed the following apparatus :—

A low tank, made of iron, wood, or stone, divided by vertical partitions into six or more compartments, each of which communicates with the next one, so that the water entering into the first travels along in a serpentine course to the last, is filled with salt; and through an opening just above the bottom in one of the corners water is admitted, which is conveyed by a pipe from the bottom of another tank. The latter is divided into two compartments: water is run into one of these, and flows into the other over the partition, which is of the same height as the partitions in the lixiviating-tank; so that the level of the water in the latter is always the same. The water flowing over into the second compartment of the water-tank runs away through a waste-pipe. On its way through the lixiviating-tank the water is converted into saturated brine of 42° Tw., and in the last compartment is diluted by a jet of water to 38° or 40° Tw. This is done because from a saturated brine, on admitting $NH_3$, crystals of NaCl separate, which are not further acted upon. The last compartment is larger than the others, and contains a filter for retaining the impurities of the brine.

Natural brine contains magnesium and calcium salts in solution which are very troublesome and hence must be removed. This is done by first precipitating the magnesia with milk of lime, and then the calcium salts by ammonium carbonate; afterwards a certain quantity of salt should be added, so as to bring up the brine to full strength. The precipitate is removed by a special apparatus in which also the continuous saturation of the brine with ammonia is automatically effected.

In fig. 3, R and R′ are tanks for brine; A is the dissolver for ammonia, communicating with R and R′ above and below by the cocks *p*, *p*′, *r*, *r*′; only one of the tanks R R′, alternately, is connected with A. Suppose this to be R, *p* and *p*′ are opened, and $NH_3$ gas is admitted through T, from the still (which will be de-

scribed hereafter), into A, where it is distributed by the perforated

Fig. 3.

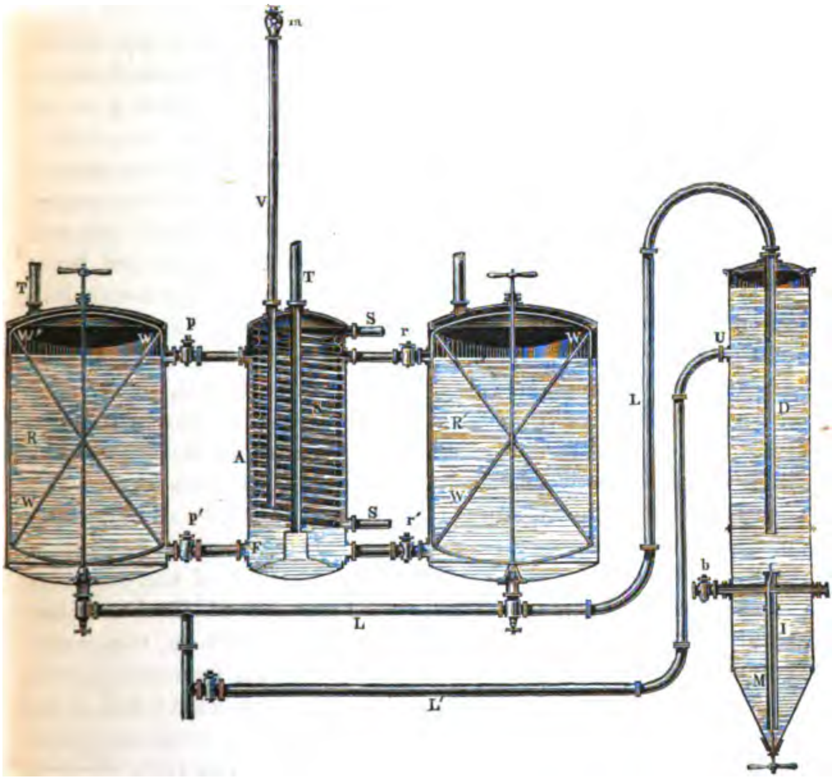
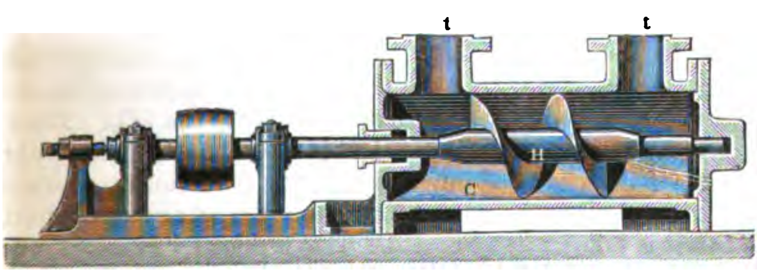



Fig. 4.




false bottom F and quickly absorbed by the solution. From R,

into which a quantity of milk of lime suitable for that special brine has been introduced, and the contents of which are agitated by W W′, the brine flows into A and back again; the circulation is produced by the agitating arms W W′, or in case of need by the screw H (fig. 4) revolving several hundreds of times per minute and interposed in one of the connecting pipes between R and A. As the temperature rises very much on the absorption of the ammonia, there is a cooling-worm S placed within the dissolver A, in which water circulates. The pipe V serves for introducing ground salt in case the brine is not strong enough—the proportions being regulated by a wheel divided into several compartments, *m*. (A special dissolver for salt is not employed here.) T′ is a pipe for the escape of air, which, being charged with $NH_3$ vapour, is carried into an absorbing apparatus. For the rarer case of a natural brine being too strong, Solvay indicates an automatical diluting-apparatus, in his patent No. 999, 1876.

The saturation of brine with ammonia must be carried to a certain point—which can be recognized by the brine, its volume being increased by saturation with $NH_3$, attaining a certain level. This can be tested by hand, and the position of the cocks altered accordingly; but of course an automatical arrangement is preferable. In 1863 Solvay availed himself for this purpose of the difference in specific gravity between the pure brine (38–40° Tw.) and that saturated with ammonia (30–25° Tw.). Following the law of communicating tubes, the brine saturated with ammonia rises to a greater height, in order to balance the pure brine; and it was only necessary to put a lateral pipe for running away the liquor, to which it must rise when its specific gravity has sunk down to 25° Tw. This principle is not available now that Solvay introduces large and varying quantities of carbonic acid at this stage of the process; by this the bulk of the liquid is increased but very little, its density very much. Hence he employs an automatical apparatus based entirely upon the increase of volume of the brine on saturation with $NH_3$, and independently of the $CO_2$. The dissolver for ammonia is connected with two reservoirs, one of which measures the brine and introduces it into the dissolver, whilst the other one draws off a corresponding quantity of ammoniacal brine when it is sufficiently saturated. This is done by means of a float in one of the reservoirs, which, when the ammoniacal brine has risen to the proper point, opens a valve by means of a lever

arrangement and allows the brine to run out, whereupon, as it descends, another valve is opened, by which the requisite quantity of fresh brine is again introduced.

It would appear that this automatical saturating apparatus, even in its new form, is not altogether satisfactory: it is very ingenious; but the play of valves and levers is somewhat complicated. At least it is not employed at Northwich, where the degree of saturation of the brine with ammonia is found by titrating. We accordingly refer for the drawing and detailed description of the apparatus to the patent-specification (No. 1904, 1876, p. 11). Actually not two, but a larger number of dissolvers for ammoniacal brine are combined to form a set.

When the brine contains enough ammonia, the agitator in R (fig. 3) is stopped; any precipitated magnesium or calcium carbonate, along with insoluble impurities of freshly dissolved salt, quickly settles down, and can be drawn off at the bottom, where the vessels are made conical and provided with mud-valves. Where large quantities of mud have to be dealt with, Solvay employs the continuous decanting-apparatus D (fig. 3). The mud, of course mixed with a good deal of liquor, is forced by means of compressed air or carbonic acid, acting upon the surface of the liquid in R, through the pipe L into the tall cylinder D; the liquid from this overflows through U; the mud remains lying in the conical bottom, from which it is scraped off by the scraper M; it again rises in the pipe I, and is run off through *b*. According to requirements, more or less of the contents of R are passed through the decanting-apparatus. Another, similar apparatus is described in the patent No. 999, 1876, p. 4.

After decantation the ammoniacal brine is filtered, in order to be obtained perfectly clear; otherwise all its impurities would pass over into the soda. Since the particles still suspended are very fine, a closely-woven cloth must be employed for filtering; and this necessitates strong pressure, which is effected by the cylinder B (fig. 5), within which a smaller cylinder O, with many perforations, is fixed. The filtering-bag is either inside O, and consequently taken out when full of mud; or it is outside, in which case the mud is removed by *d*.

The perfectly clear ammoniacal brine must now be cooled down very strongly before being treated with carbonic acid. This is done, in addition to the preliminary cooling by the refrigerating-

coil S in the cylinder A (fig. 3) by means of a cooling-apparatus C (fig. 5), composed of concentric tubes, like a Liebig's cooler. The inner tubes communicate alternately at their ends by bends *z'*; the outer pipes also alternately at both ends by the straight pipes *z*. The best way is to run the cooling-water in the inner tube *z'*, and the brine in the annular space, so that it enters through *h* and leaves through *h'*; it can thus be cooled once more by water running outside all over the apparatus. The cooler need not be placed below the dissolver A, but may be alongside of it, since the liquids have, in any case, to be forced onward by compressed air or carbonic acid.

A self-acting pressure-apparatus, which at the same time serves for measuring the liquid, is represented in fig. 6. The liquid

Fig. 5.

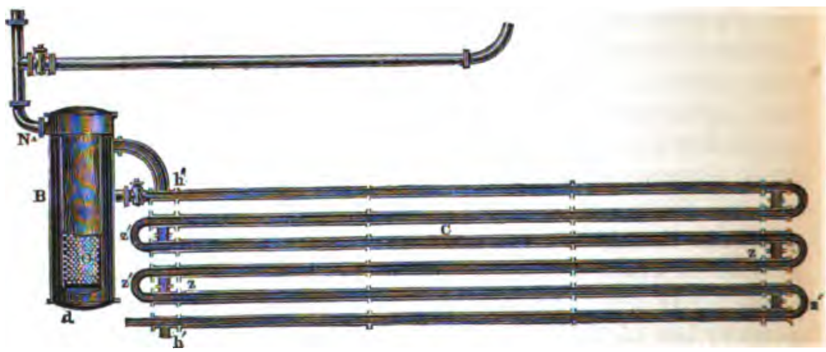
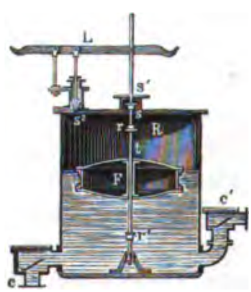



Fig. 6.



flows through the valve-box *c* into the vessel R; with this the float F rises until it touches the washer *r* fixed upon the rod *t*, which it raises, and with it the valve *s*, by which the opening *s'* is closed. *t* also acts upon the lever L, which raises the valve $s^2$ and admits into the apparatus compressed air or gas, which forces out the liquid through the valve-box *c'*. The float F descends with the liquid till it comes into contact with the washer *r'*, and draws down the rod *t*, which closes the admission of compressed gas and opens the valve *s* for the escape of compressed gas through *s'*. Fresh liquid then enters through *c*, and the operation begins over again. An ordinary meter applied to the lever L indicates the number of times the lever has been worked, and with it the volume of the liquid forced. This apparatus works very well, and is in constant use.

As an *absorbing apparatus for treating the ammoniacal brine with carbonic acid,* Solvay formerly employed an apparatus in several compartments with horizontal shelves and perforated false bottoms. The gas ascended from the bottom to the top; the liquid entered the middle compartment, rose through a pipe to the top compartment, and at last passed through the bottom compartment, the shelves in the different compartments compelling the liquid to travel a long way round. As this apparatus worked but slowly, Solvay constructed another, of which fig. 7 is a vertical section. In this cylindrical tower A there are a number of finely perforated plates *b b* of the shape of a spherical segment (shown in figs. 8 and 9 in section and top view), and also a number of plates *c c* with only one or a few holes, which just allow the gas and the saturated solution to pass, but do not permit the freshly entering liquid to mix with that at the bottom, which is nearly saturated. In the margins of the perforated plates nicks are made, so that the liquid and the gas can pass through them when the holes have got partially stopped up. In fig. 10 some of the plates are shown on an enlarged scale, in order to exhibit the guide-rods G, which allow a little play to the curved plates. This tower is always kept nearly filled with liquid, whilst carbonic acid is forced in at the bottom through the pipe B by means of a blowing-engine. By this the gas is not only brought into intimate contact with the liquid meeting it, but by its expansion also performs a considerable amount of mechanical work, and thus absorbs such a large quantity of heat that the liquid is prevented from becoming heated, as

Fig. 7.

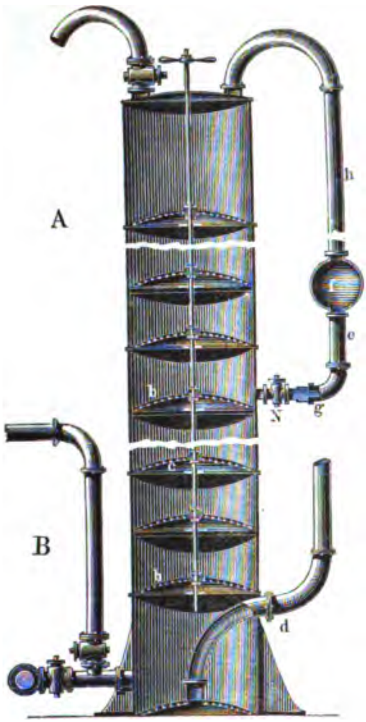



Fig. 8.


Fig. 9.

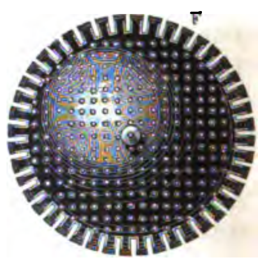
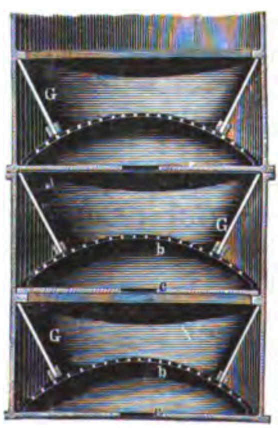



Fig. 10.



it would otherwise be by the heat evolved by the absorption of the $CO_2$ by the $NH_3$; this, according to Solvay, cannot well be avoided in any other way. The liquid enters at about half the height of the cylinder by the pipe *e*, into which it flows from a tank *f*, so that its level is always kept at the same height, about 10 feet below the top of the cylinder. The valve *g*, which opens inside, prevents the liquid, in case of a stoppage, from running out of the tower. The vessel *f* is closed, and connected with the upper end of the tower by a pipe *h*, which keeps the pressure equal in both. The same vessel *f* may feed several absorbing-towers. In this way only the upper half of the liquid is renewed; it descends very slowly, and, since it is soon saturated with carbonic acid, is adapted for receiving all the $NH_3$ which the gas may bring from the lower part of the tower. The towers must be high enough to absorb at least half of the $CO_2$ entering below, at the same time converting all $NH_3$ contained in the liquid into bicarbonate. A height of from 36 to 53 feet, which compels the gas to be forced in at a pressure of $1\frac{1}{2}$ to 2 atmospheres, gives the best results. Actually 15 cylinders are superposed upon one another, each 1 metre high. It is best not to admit the gas in a continuous jet, because the irregular motion prevents the precipitated bicarbonate from settling at one side. Still the small holes of the plates get stopped up from time to time by a crust. The tower is then emptied, filled with water, steam blown in; and when the crust is completely dissolved, the liquid is run out; then the tower is filled from another with liquid, and the operation started again.

The carbonic acid for this apparatus is obtained from two sources:—in the first place, from the conversion of the bicarbonate into monocarbonate: this, theoretically, would yield half the $CO_2$ required; but since the $CO_2$ of the bicarbonate cannot be recovered completely, the much larger portion of carbonic acid must be procured in another way, which is at once afforded by the burning of the lime required for recovering the ammonia (see below).

The lime-kilns are of the usual construction, with their lower portion contracted; the heat is generated by lateral coke fires; and the whole is surrounded by an iron shell. Powerful blowing-engines, which consume most of the coal required in this process, suck the gas away from those kilns; before reaching the blowing-cylinders, it must first pass through iron coke-towers, in which a stream of water at the same time washes and cools the gas. In

the engines the gas is compressed to $1\frac{3}{4}$ atmosphere, which heats it again considerably; but as the process peremptorily requires a low temperature, the gas is next made to pass through cylinders into which cold water is injected. By simple separators the water is separated from the gas, and the latter conveyed to the absorbing towers, so far as it is not employed directly in the ammonia-stills, the dissolvers, &c. The gas is made richer in $CO_2$ by directing from time to time a strong jet of steam upon the red-hot limestone, which, as is well known, liberates carbonic acid from it.

The gaseous mixture coming from the lime-kilns contains up to 30 per cent. (on the average at least 25 per cent.) by volume of carbonic acid. It is so far utilized in the absorbing-towers that it escapes with 10 per cent. $CO_2$. But as it always contains some ammonia, it must pass through an apparatus in which it is washed with brine, which it at length entirely saturates with ammonia; the washed gas now escapes into the atmosphere. In order to render this washing-out of the ammonia more effective, the patent No. 1904 (1876), p. 12, prescribes introducing brine at the top of the tower, mixed with a little solid salt (which in the presence of $CO_2$ is soluble in the ammoniacal brine); the greater concentration thus produced causes a larger separation of bicarbonate at the bottom of the tower. (It would appear that in practice the washing of the gas with brine did not take place in the tower itself, but in a special apparatus.)

In the absorbing-towers there is again much heat evolved by the reaction between the ammoniacal brine and the carbonic acid, and the separation of solid sodium bicarbonate. But as the process, to be completely successful, requires by all means a low temperature, not merely (as described above) are both the ammoniacal brine and the carbonic acid previously cooled as much as possible, but cooling must accompany the absorbing process as well. This is partly effected by a copious stream of water running upon the towers and down their sides, and partly by the circumstance that the gases from the blowing-engine, compressed to $1\frac{3}{4}$ atmosphere over and above the ordinary pressure, expand in the apparatus till the latter pressure is reached; this takes place with considerable absorption of heat.

Much stress is laid by Solvay (patent No. 2143, 1876, p. 4) upon the point that the largest portion of the heat is generated during

the first stage of the action of $CO_2$ on the ammoniacal brine, when the liquid is only partly saturated with $CO_2$; later on, much less heat is given out. Now the first carbonization of the ammoniacal brine may be effected very easily without employing any special means, without the tower; and if this is done and the liquid properly cooled, the tower is much less charged with evolved heat. At the same time the gaseous current within the tower carries away less of ammonium carbonate than of free ammonia. Hence Solvay introduces washed and cooled $CO_2$ into the upper portion of the ammonia-still; so that the ammonia arrives in the "dissolver" already in the state of carbonate; its heat is communicated to the ammoniacal brine, and is carried off again by the refrigerating-coil and the annular-pipe cooler.

Every half hour a certain portion of the contents of the absorbing-towers is drawn off, and the pasty mixture separated into a solution of ammonium chloride with a little carbonate and sodium chloride, on the one hand, and solid sodium bicarbonate on the other. This is done by some of his predecessors and by Honigmann with the assistance of centrifugal machines. Solvay, however, prefers vacuum filters, consisting of iron cylinders of about 10 feet diameter and 5 feet high, in which the filtering material lies upon a grating. It is a linen or woollen fabric, covered by a wire gauze or a finely perforated metal plate. Below this strainer a vacuum is made by an air-pump, and the mother liquor sucked off very quickly; water is now squirted by a rose very uniformly over the fine-grained bicarbonate; and this is continued till the salt smells little or not at all of ammonia. According to the patent No. 1904, p. 13, the water is to be applied warm, in order to dissolve any sal-ammoniac crystals more certainly. It is not possible, however, to remove all the ammonia by washing the salt without dissolving much bicarbonate; and this is a source of loss of ammonia. Or else the liquid may be heated, after being run out of the tower, in order to dissolve any sal-ammoniac crystallized out.

In the patent No. 999 (1876), p. 5, Solvay describes an arrangement for uniformly dividing the bicarbonate and washing it by means of a turbine, and a peculiarly constructed vacuum-pump with water piston. In No. 1904, p. 13, he gives a detailed description and drawing of a continuous filter, consisting of a turntable, divided into eight sectors, each of which is fitted as a filter; here all stages of filtering and washing are carried on at the same

time, since by the revolution of the turntable each sector receives successively fresh liquor from the absorbing-towers, weak washings, and fresh water, and the corresponding liquids are run away separately. The author has not seen this somewhat complicated apparatus at work.

Now follows the *drying of the bicarbonate, and its conversion into monocarbonate, i. e.* ordinary soda ash. In the state of bicarbonate it can only be employed to a very small extent, both because there is a very restricted demand for this article (comp. Chapter XI.) and because the ammoniacal bicarbonate obstinately retains a smell of ammonia and hence is difficult to sell. For this purpose the temperature employed in drying should not exceed 59° C. The task of converting the bicarbonate into monocarbonate and recovering the liberated $CO_2$ and $NH_3$ seems to be a very simple one, but in reality is very difficult, as is proved by the large number of patents taken out by Solvay for this operation, a few of which we will describe.

In a vertical cylinder, G G (of which fig. 11 is a sectional elevation, and fig. 12 a sectional plan), there are a number of round plates H, with openings at the circumference and in the centre. A perpendicular shaft, I, passes through the top and bottom of the cylinder and carries arms K K, with scrapers L L, which move the mass lying on the plates alternately to the periphery of one and the centre of the next lower plate, so that it ultimately gets to the bottom of the cylinder. The plates themselves are hollow, and are heated by steam or hot gases through the pipe *m m*. The bicarbonate is charged by a hopper M, in which arms O are slowly turned round by the shaft N; it is always kept full, so that the $CO_2$ cannot escape. The dried mass arrives at the bottom of G in a finely-ground state, ready for packing. The gases driven off in drying escape by a pipe R in the top. If hollow plates are to be dispensed with, the gas can be conveyed directly into the cylinder. [It will be seen that this apparatus is quite similar to MacDougall's pyrites-small burners (Vol. I. p. 222). It is said not to work very well.]

Another drying-apparatus for soda is shown in figs. 13 and 14; it is an iron pan A, closed by a cover through which a perpendicular shaft B passes in a gland. The latter carries arms C, with scrapers D, which stir round the bicarbonate, the pan being heated to the proper degree by a fire below. The most recent

Fig. 11.

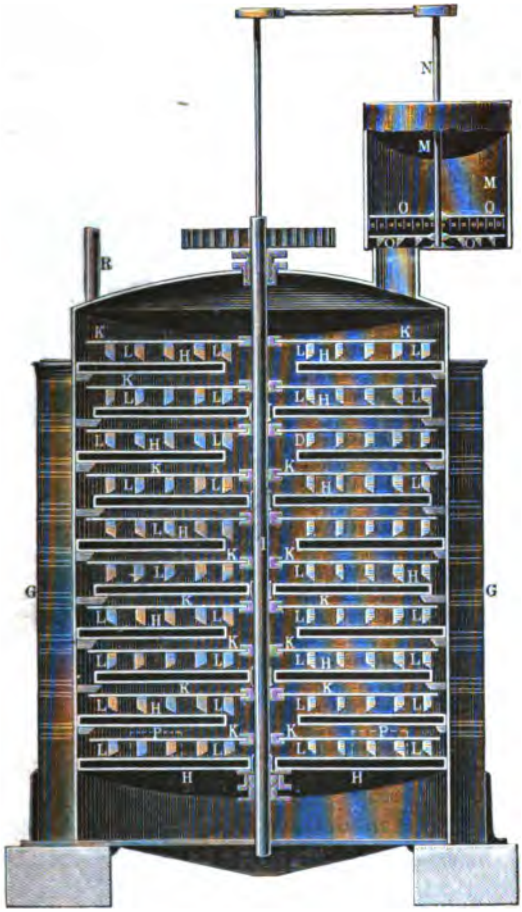



Fig. 12.

construction of scrapers is shown in figs. 15 and 16. *c* is the scraper itself, which has a certain amount of play round the

Fig. 13.

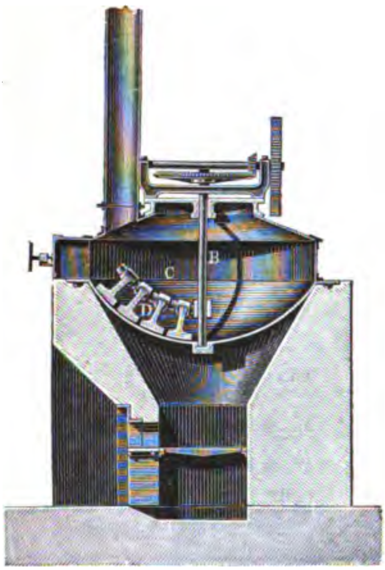



Fig. 14.


Fig. 15.

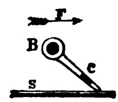
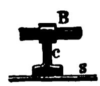



Fig. 16.




revolving shaft B; S is the surface to be scraped; and the arrow F shows the direction in which the scrapers move.

In No. 2143, p. 5, there is a description of an apparatus for decomposing bicarbonate by steam, which does not seem to have found any practical application. Neither does this seem to have been the case with the following chemical means for decomposing the bicarbonate—viz. passing ammonia gas or ammoniacal brine through it, applying heat, when the liberated $CO_2$ is at once to be retained by the $NH_3$, Solvay himself has returned to driving off the $CO_2$ by heat alone, and, according to the same patent, employs a cylindrical furnace somewhat inclined (figs. 17 and 18), consisting of an iron shell and a brick lining which is slowly turned round by the cog-wheels E and *e*; it is supported on friction-rollers *r* and *r'*. F is a kind of gas-generator; T, the hopper for introducing coals; B, the pipe for supplying the bicarbonate; C, chamber for collecting the calcined soda-ash.

n/ At the Northwich works the bicarbonate is first subjected to a

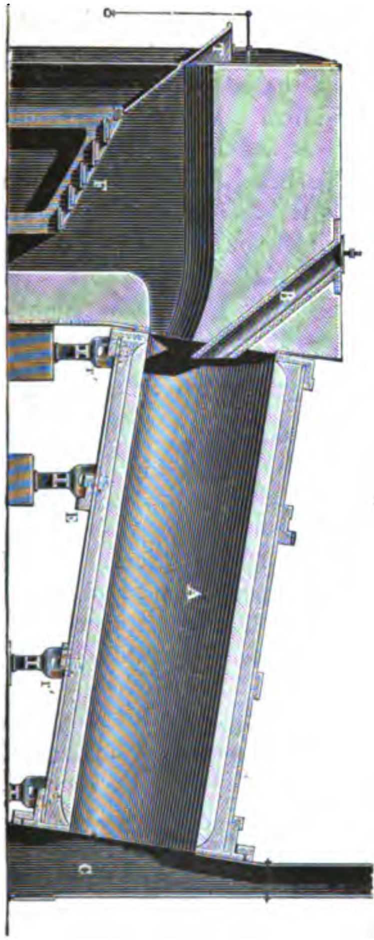


Fig. 17.

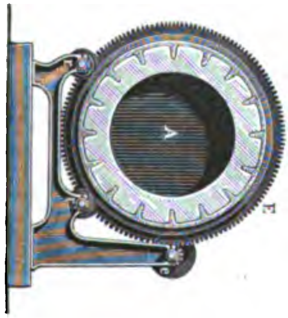


Fig. 18.

comparatively low temperature in a closed roaster, within which a perpendicular shaft revolves with horizontal arms and scrapers sweeping its bed; but the operation is always finished in other closed roasters (muffle furnaces) where the soda ash is brought to a bright-red heat by gaseous fuel. Thus it becomes much denser than that (Solvay's) finished at a low temperature. By mechanical pounding in the casks it becomes still denser, but never quite so dense as calcined ash made by Leblanc's process.

The gas driven off in all these apparatus is conveyed by an air-pump into a washing-apparatus, which retains all the ammonia contained in it; the carbonic acid is reconducted into the absorbing-towers.

Solvay has recently patented (No. 2687, June 12, 1877) the following process for obtaining soda ash in a dense form for melting-operations. The damp bicarbonate is continuously or gradually put into the funnel E (fig. 19), and from this gets into the trough C. Here some monocarbonate is formed. $CO_2$, $NH_3$, and steam are conveyed away by the pipe T. The shaft A, moved by a cog-wheel, carries two arms F F, to which the scrapers R are attached on a swivel joint; these prevent the sticking of the mass to the trough. While the soda is descending in the retort G, it is heated up to the melting-point, and can be run off through the openings O and O′. When it runs off through the opening O′, the impurities settle in front of the lower opening O, and can be removed through it. H is the fire-grate; I and K, smoke-flues.

Figs. 20 and 21 show another arrangement of the apparatus, in which the retort has another shape, and is provided with the pipe *t* for running off the soda. *b b* are fire-bricks, distributing the flame to make the temperature of the apparatus more uniform. Fig. 22 shows an apparatus without machinery. The soda or bicarbonate is put into the hopper E, till the vessel C is filled. The melted mass runs off through *t*; $NH_3$ and $CO_2$, along with steam, escape by T. Within C the bell X can be placed, in order to diminish the thickness of soda to be heated. The vessels for melting the soda can be made of cast or wrought iron, steel, or other metal, and protected against the oxidizing action by a coating of fireclay or a paint of borax solution &c.; or the non-oxidizing flame of a Siemens furnace may be employed; or the part of the apparatus in which the soda melts can be made of silver or silvered.

Fig. 19.

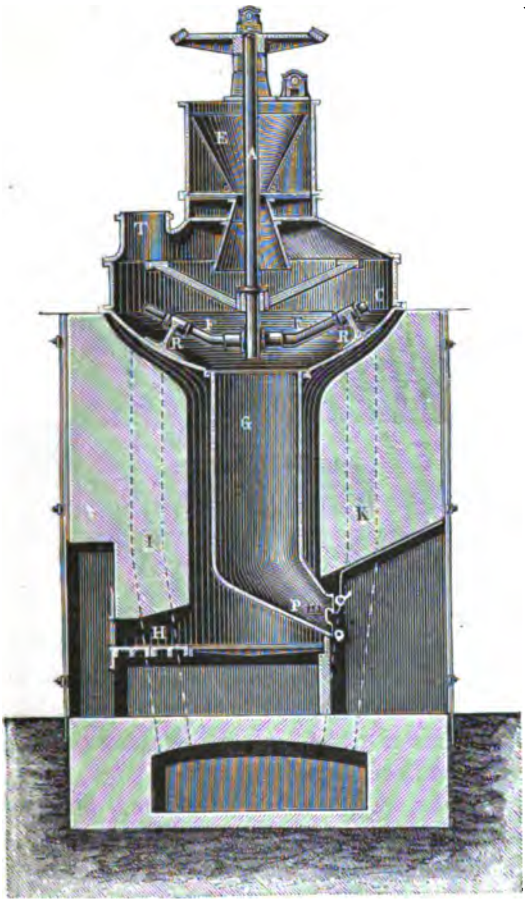
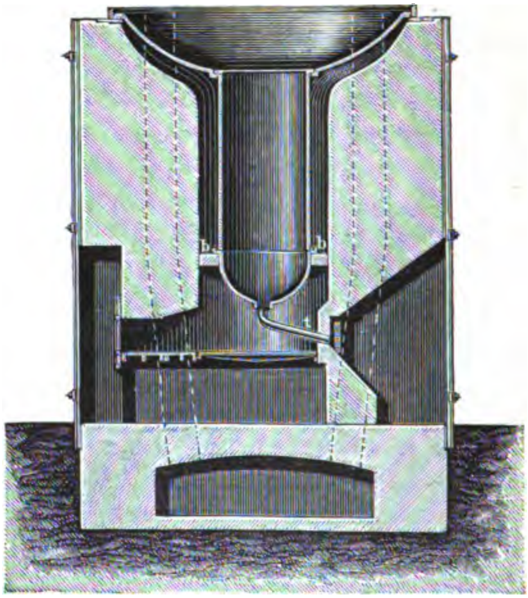



Fig. 20.

Fig. 21.

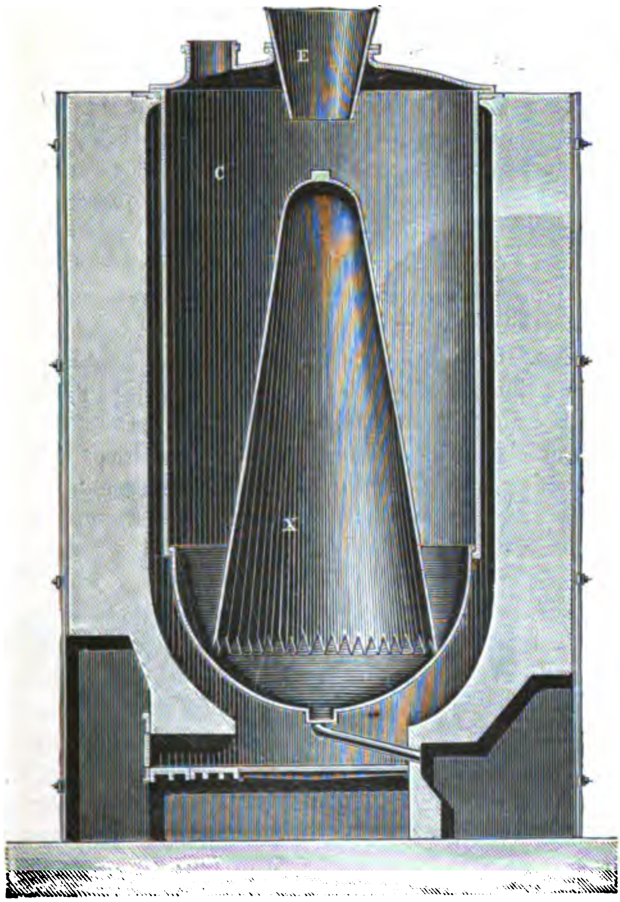



The simplest plan for cooling the soda run out is by squirting so little water upon it that the water evaporates at once without being absorbed by the soda. If it is to be granulated, it is run upon a revolving metal plate, and at the same time a small jet of water (as just mentioned) is run upon it.

In order to make soda ash containing a little caustic (similar to the "sels caustiques" of French works), a steam jet is forced through the melted soda or upon its surface. This expels some $CO_2$ and generates NaOH, which can be continued up to the desired point; in the continuous apparatus the steam jet must be continuous as well, and regulated according to the degree of causticity desired. The steam-pipe is shown in fig. 19 at P; its end is perforated with small holes. When employing the apparatus fig. 21 or 22, the soda is best first run into a vessel, where it is kept in the liquid state, and there treated by steam.

In order to make soda of weaker strength, Solvay soaks it with brine before drying it; or a sufficient quantity of water is incorporated with it by contact at the ordinary temperature. [In many cases neither of these plans will be allowable.]

Fig. 22.

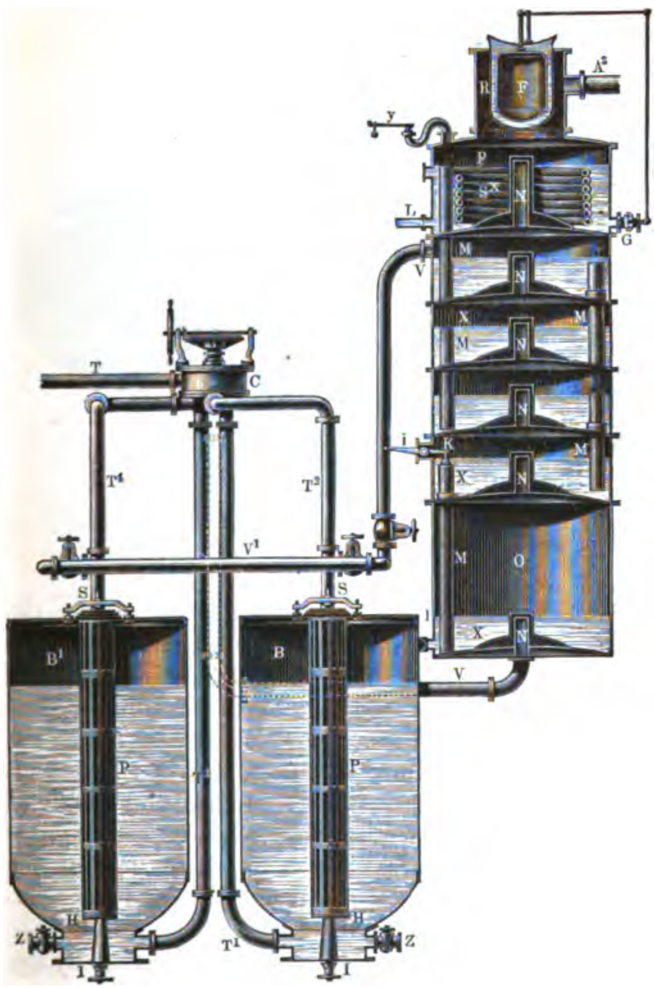



We must now describe the *recovery of ammonia* from the ammonium chloride formed. The solution, filtered from the sodium bicarbonate, contains along with $NH_4Cl$ some ammonium bicarbonate, an excess of common salt, and some free carbonic acid [besides evidently as much sodium bicarbonate as will be soluble under these circumstances.] Hence it need only be heated with lime to furnish ammonia. For this purpose Solvay, in his first patent, described an apparatus consisting of a long iron cylinder, one end of it, A, was heated by boiling water or an open fire, in the

middle portion, B, where the boiler widened out towards the top, finely ground lime was introduced by a mechanical contrivance, and the mixture carried back to A, where it was subjected to heat; $NH_3$ was given off, which first passed through B and then into the other end, C, which was bent up in the shape of an elbow; here it was cooled by water from the outside, and deprived of a large portion of aqueous vapour; at last it escaped by a pipe into the apparatus, where it was absorbed by brine; the $CaCl_2$ liquor was run away by a pipe from the hot part of the apparatus.

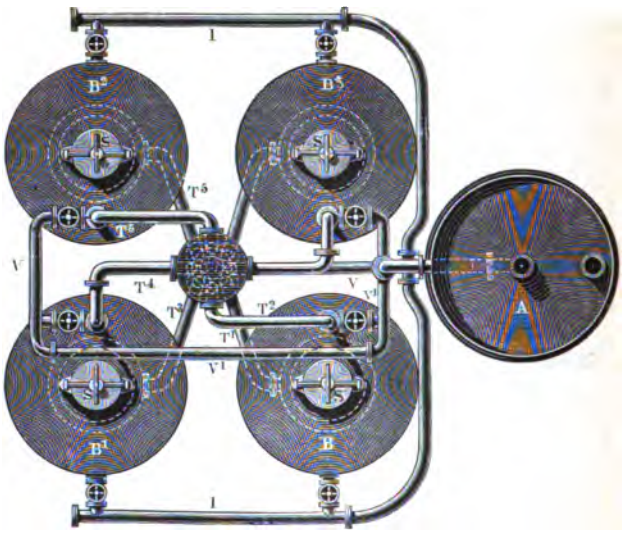
In the patent of 1872 there is only the statement that Solvay recovers the ammonia by the ordinary well-known methods. The apparatus serving now for distilling the ammonia is described in the patent No. 1904 (1876), p. 6. It is founded mainly upon the well-known principle of spirit-rectifying apparatus; but it allows first the $NH_3$, already present as such or as carbonate, to escape before the quicklime is introduced, and it utilizes the heat generated in slaking the latter for distilling the ammonia; so that, besides this and the exhaust-steam of the engines, no special source of heat need be applied. Figs. 23 and 24 are a section and a plan of the apparatus. The liquor filtering from the bicarbonate first passes through the column A for distillation without lime, and then the four stills B to $B^3$ for distilling with lime. The stills B, $B^1$, $B^2$, $B^3$ communicate with each other by a distributor C, similar to those used in gas-works, which permits any boiler to be isolated without interrupting the distillation in the others. As a rule, one still is stopped for discharging and charging, while the other three are working. The exhaust-steam from the engines passes through the pipe T into the distributor C, and from this by $T^1$ to the longest-working still B; from here it comes out by $T^2$, again into the distributor C, and passes through $T^3$ into the second still $B^1$. Similarly it passes into the last-filled still $B^2$; so that fresh steam enters just that still the liquor of which has only to be deprived of the last traces of $NH_3$. When the steam leaves the last still $B^2$, it again enters the distributor and passes through V into the distilling column A, where it causes the expulsion of the ammonia present as such or as carbonate. In this column the mother liquor from the bicarbonate running down acts so that the steam is condensed, while the $NH_3$ passes on, and the mother liquor receives a preliminary heating. The last cooling is effected in the upper part of the column by the refrigerator P, so that

Fig. 23.



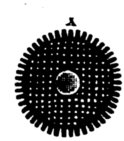

from the pipe A³ only gaseous ammonia with some ammonium carbonate escapes, but no steam—which is very important, since the gas from here passes direct into the "dissolvers" for brine, and this must not be diluted with water. Within the refrigerator P is the cooling-coil S, filled with liquid to be distilled, which thus receives a first heating. On the top is a regulator, consisting of a float F in a vessel R, filled with a little water.

Fig. 24.



This water is more or less heated by the gas passing through; the warmer it is, the more the float descends, and ultimately opens a cock G, which admits fresh liquor into the coil—or in the same way as the admission of steam into the distilling-apparatus is regulated. From the coil the liquor runs out by L into the interior of the distilling column, and from this by *l* into that one of the lower stills which has just been emptied and freshly charged with lime. When just as much liquor has collected in the lower part O of the column A as suffices for filling one of the stills, which can be seen by means of a gauge-glass, the valve K is closed by the lever *i*, and a further descent of liquor into O prevented. Otherwise the liquor in the column always runs off by the overflow M, whilst the central pipes N convey the $NH_3$ gas and the steam. The convex false bottoms X, separately drawn in fig. 25, serve for distributing the steam in the liquid; they are perforated with many conical holes, and are nicked all round. *y* is a safety-valve at the end of a swan-neck pipe filled with water or petroleum, which prevents the $NH_3$ from corroding the metal of the valve.

Fig. 25.



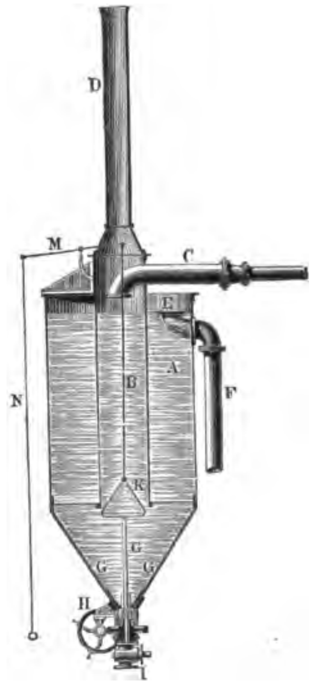
In the stills B to $B^3$ the ammonium chloride must be decomposed by lime. For this quicklime, straight from the kilns, is put through the doors S into the central (or lateral) cages *p*, which retain the unburnt pieces, stones, &c. The $NH_4Cl$ liquor ascending in the still B slakes the lime; and the heat thereby evolved assists in the distillation: this can never take place with such violence as to cause any danger, since in this case the evolved gas and steam would force back the liquor and not permit it to enter into the cage. Thus the heat of the slaking lime and that of the exhaust-steam from T act at the same time.

Solvay in the same patent describes another apparatus for continuous distillation with a single column. This does not seem to be actually employed.

At the end of the distillation the exhausted liquid is run off by the cocks *z*; and the bottom door I, which at the same time supports the bottom of the lime-cage *p*, is opened, so that the residue falls out of the latter. In order to separate the liquor, containing calcium and sodium chloride, from the suspended matter (if it is intended to be utilized), Solvay passes it through the self-acting decanting-apparatus, fig. 26. The hot liquor passes through the pipe C into a central pipe B, whence the steam escapes through the pipe D, while the liquor rises up in the vessel A and at the top runs over into the pipe F at E. The lime mud settles at the bottom, is scraped off the same by scrapers moved by the hand-wheel H and taken out at I. The conical valve K, moved by the lever M and the rod N, prevents the fresh liquor from disturbing the settled lime mud. The distillation is best carried on in a partial vacuum, produced by connecting the outlet $T^V$ of the dissolvers (fig. 3, on p. 9) with a water-piston pump; the gas, before reaching the pump, first passes through washing-apparatus for retaining any ammonia it may contain.

The *loss of ammonia* (a matter of the greatest importance to this process) is very unequal: sometimes it rises to 20 per cent. of ammonium sulphate on the carbonate produced; sometimes it falls to 3 per cent. At Northwich it was stated to the author at 8 per cent. In Solvay's own works it formerly (in 1874) amounted to 8·75 per cent., latterly only 6 per cent.; and quite recently it is said to have come down to 4 per cent.: according to the opinion of those most competent to give one, the last mentioned is probably the minimum loss to be expected in any case.

Fig. 26.




The *calcium chloride* solution from the ammonia-stills is nearly always run to waste, as there is extremely little use for this article. In it all the chlorine of the common salt is wasted; and this is one of the principal drawbacks of the ammoniacal soda-process.

In his 1872 patent, Solvay proposes, for places where hydrochloric acid is valuable, to employ *magnesia* or *magnesium oxychloride* in the place of lime for distilling the ammonia. The solution of $MgCl_2$ remaining after the distillation is boiled down to dryness, and the residue heated in a current of steam till no more HCl escapes. The latter is condensed or employed directly for generating chlorine. Magnesia remains behind, and is used over again, after washing, for distilling ammonia. In this case also the common salt left undecomposed is utilized.

This idea is not due to Solvay, but to Weldon, who in 1872

had also patented it; his soda process of 1866, expressed by the equation

$$2\,NaCl + MgCO_3 + CO_2 + H_2O = 2\,NaHCO_3 + MgCl_2,$$

already foreshadows it. In 1873 Weldon also patented the use of magnesium carbonate in order to prepare ammonium carbonate directly from the $NH_4Cl$—which Young had done already in 1872, but without describing, as Weldon did, the recovery of $MgCO_3$ from the $MgCl_2$ by heating it up to the expulsion of HCl, suspending the MgO in water, and passing $CO_2$ into the mixture. The reactions which take place are as follows:—

$$\begin{aligned} &(1)\quad MgCl_2 + H_2O &&= MgO + 2HCl\,; \\ &(2)\quad MgO + CO_2 &&= MgCO_3\,; \\ &(3)\quad 2\,NH_4Cl + MgCO_3 &&= MgCl_2 + (NH_4)_2CO_3. \end{aligned}$$

The first reaction, however, does not take place as smoothly as on paper: magnesium oxychloride always remains in the place of pure MgO; and hitherto the cost of labour, fuel, and wear and tear of apparatus has always exceeded the value of the muriatic acid obtained.

According to some new English patents of Solvay's (of Jan. 8th, 9th, and 12th, 1877), hydrochloric acid is to be obtained from calcium chloride by the process, already proposed by Pelouze, of igniting it with sand, clay, &c. As far as can be learned, this process, owing to the small yield of HCl, has even less prospect than the magnesia process of the muriatic acid obtained paying the costs, let alone leaving a profit. We have touched upon these patents already in the 6th Chapter of Book II. (Vol. II. p. 172); the part referring to chlorine will follow in Book IV. Here we will only mention that the silicates and aluminates of calcium and magnesium, obtained in this process, were to be re-employed for the ammoniacal soda-process by heating them with the $NH_4Cl$ solution: thus $NH_3$ and $CaCl_2$ (or $MgCl_2$) and alumina (or silica) would be obtained; so that even the lime for recovering the $NH_3$ would be saved. *If* these processes were to prove successful, the Leblanc process could not for a moment compete with the ammonia process; but this *if* so far has not come to pass.

Solvay's process is an attempt to combine the elements of a

continuous, self-acting, circular process, avoiding manual labour to the utmost. A thorough mutual action of the gases and liquids is brought about by causing them to meet in a systematic way by increasing the pressure, well distributing the gas, completely cooling the gases and liquids; it also secures in a very ingenious way a self-acting regulation of the level of the liquids. Altogether Solvay's manufacturing-apparatus is a machine, of a very ingenious but complicated kind, which requires to the utmost the continuous supervision of the mechanical engineer, in order to prevent losses, but claims the attention of the chemist only in a subordinate degree.

The soda ash made by Solvay, as well as any other ammonia-soda, is very pure, inasmuch as only the sodium salt is precipitated from a saturated brine, and not the calcium salts etc. of the mother liquor. It is, of course, absolutely free from caustic, sulphide, and iron, and of very high strength, viz. easily up to 98 or 99 per cent. real $Na_2CO_3$. Nor, in a sanitary point of view, should it be forgotten that in this manufacture no noxious gas whatever is given off; and no troublesome by-products are formed.

One drawback, objected to Solvay's and any other ammonia-soda, is that it is too voluminous, and, owing to this, is inferior for melting-processes to Leblanc soda: *e.g.* the pots in glass or ultramarine works cannot receive the same weight of charge as with ordinary soda ash; and, owing to the greater porosity of ammonia-ash, the heat penetrates less easily to the interior of the charge*. Probably for this reason, the ammonia-soda on the Continent commands a comparatively lower price than Leblanc ash, in spite of its excellent quality. Some ultramarine-makers report unfavourable results consequent upon using this soda (Curtius, in 'Chemische Industrie,' 1879, p. 116). In some cases also the NaCl contained in the former is objected to; but this can only be done

* It has been doubted whether ammonia ash is really inferior to Leblanc ash in this respect; but Fürstenau (Chemiker-Zeitung, 1879, p. 441) has proved that, in fact, not only is ammonia ash far more voluminous than Leblanc ash, but it also shrinks on being gently heated, which Leblanc ash never does. Those descriptions of ammonia ash which do not shrink too much, say from 8 to 7 volumes, can be used very well in the manufacture of ultramarine (no doubt also for glass-making &c.); but other descriptions, shrinking from 16 to 12 vols., cannot be so employed.

in comparison with the purest Leblanc soda, since ordinary English 52-per-cent. ash contains about 2 per cent. NaCl (that is, more than the percentage of all the impurities of the best ammonia-ash put together). As to the rest, some ultramarine- and glass-makers state that they get excellent results with ammonia-ash; and Solvay, as we have seen (p. 22), constantly strives to improve the density of his ash. Reinhold Hoffmann, however, one of the foremost ultramarine-manufacturers in Germany, states that even the so-called "dense" soda of Solvay does not, by far, equal in density the ordinary soda ash, and has consequently been abandoned again by the German ultramarine-manufacturers, since, as regards purity, the German alkali-manufacturers [like some of the English] are now producing Leblanc soda of 98 per cent. $Na_2CO_3$, fully equal in every respect to ammonia-soda. The latter is entirely free from sulphur compounds, but contains some sodium chloride and insoluble impurities. The struggle is now not one of purity, but merely of price; and so far the Leblanc soda is holding its own.

The cost of plant of a works on Solvay's principle is very considerable. He states it himself at £1600 for every ton of soda ash produced per diem; but, according to authentic statements, the capital required, inclusive of land, in most places exceeds the above by 50 per cent. One of the above-described absorbing-towers turns out about 2½ tons soda ash in twenty-four hours; each tower requires one dissolver and one ammonia-still; one lime-kiln serves for four towers.

Solvay's ammonia process is only carried out by himself at Couillet in Belgium and at Varangéville-Dombasles near Nancy, and by Messrs. Brunner, Mond, and Co., at Northwich and Sandbach. According to Solvay's statements (1878), he turns out at Couillet 7500 tons, at Dombasles 20,000 tons per annum; at Northwich 20 to 25 tons, at Sandbach 15 tons per diem are made.

The following are analyses of ammonia-soda made by Solvay's process at the above works :—

| | Solvay soda. | | | English soda. | |
|---|---|---|---|---|---|
| | List. | Lunge. | Hanrez. | Pattinson. | Benrath. |
| Sodium carbonate ... | 96·23 | 95·65 | 99·438 | 98·72 | 93·84 |
| „ chloride ...... | 0·64 | 3·22 | 0·21 | 0·54 | 1·17 |
| „ sulphate ...... | 0·02 | 0·31 | ...... | 0·20 | 0·47 |
| Magnesium carbonate | trace | ...... | ...... | 0·04 | 0·17 |
| Calcium carbonate ... | ...... | ...... | trace | 0·13 | 0·16 |
| Ferric oxide ............ | ...... | | ...... | 0·01 | 0·016 |
| Alumina ............... | ...... | 0·07 | trace | 0·01 | 0·10 |
| Silica..................... | ...... | | 0·04 | 0·09 | ...... |
| Other insoluble matters | ...... | ...... | ...... | ...... | 0·23 |
| Moisture ............... | 3·11 | 0·55 | 0·31 | 0·32 | 3·74 |

A calculation made by Solvay himself in 1874 for the south of France states the following as the cost of 1000 kilog. (nearly 1 ton) of soda ash of 57 to 58 per cent. available soda, assuming a yearly make of 3000 tons :—

| | | | | francs. | | francs. |
|---|---|---|---|---|---|---|
| 1942 | kilog. | rock-salt ............... | @ | 21 | = | 40·78 |
| 87·5* | „ | ammonium sulphate . | @ | 350 | = | 30·60 |
| 2155 | „ | limestone ........... | @ | 2·50 | = | 5·39 |
| 1698 | „ | coals ................. | @ | 23 | = | 39·05 |
| 250 | „ | coke ................. | @ | 40 | = | 10·32 |
| | Labour ...................... | | | ...... | | 15 |
| | Repairs ....................... | | | ...... | | 11 |
| | Amortization and general expenses.................... | | | ...... | | 15 |
| | Casks ......................... | | | ...... | | 13·42 |
| | | | | | | 180·56 |
| | Patent-royalty .............. | | | ...... | | 30 |
| | | | | | | 210·56 |
| | | | | | | or about £8 8s. |

* Only 34 kilog. are said to be used now; but the price of sulphate of ammonia is generally very much higher than assumed above.

In a new patent of 1879 Solvay describes a number of important novelties, which we will mention all together in this place *. He now causes the lime to be slaked by a solution of calcium or ammonium chloride, whereby it assumes a granular form and is much more ready than the ordinary hydrate to decompose the solution of ammonium chloride. This is effected by running that solution through a tower filled with the "granular" hydrate of lime, and distilling off the ammonia in another apparatus.

For saturating the brine with ammonia, he now employs much larger vessels, of which the first serves for the saturation itself, the ammonia gas meeting a continuous stream of brine. The latter, becoming turbid in this action, flows over into a second large tank, where the mud settles down, and whence it is drawn off from time to time and deprived of ammonia by distillation. The clear liquor flows over into a third large tank, in a pipe reaching to its bottom and perforated all along; thus the liquid runs out at different heights into that already contained in the tank, and both become intimately mixed. In this way liquors containing mostly an equal and always a similar percentage of ammonia are obtained, which is the principal object of the new arrangement.

If the brine contains much magnesia, this can be completely separated by the addition of sodium carbonate, an excess of which does no harm.

The conversion of bicarbonate into monocarbonate seems to offer considerable difficulties; for Solvay's last patent contains the description of a new continuous apparatus, constructed almost entirely like Cammack and Walker's mechanical salt-cake furnace (comp. Vol. II. p. 110). But only longer experience can show whether Solvay has really surmounted the mechanical difficulties in the way of carrying out that, doubtless, very ingenious principle.

The waste liquors from distilling the ammonia, containing all the calcium chloride and very much sodium chloride, are to be utilized by boiling down in a tubular boiler of Solvay's own construction, or in a semicircular pan with a mechanical fishing-arrangement, very similar to Thelen's pan (Vol. II. p. 502). The common salt separates during the boiling, and is continuously fished out; the remaining liquor is run into moulds, in which the calcium

* Because the patent did not appear until the preceding text was already in type.

chloride solidifies. In order to prevent incrustations of lime, some hydrochloric acid is to be added to the liquor.

The salt is washed in a long trough containing two longitudinal shafts revolving in opposite directions and each provided with a worm, by which the salt is carried in one direction and the washing-water in the opposite one—or else in a series of small troughs, provided with scrapers and fulfilling the same purpose. The same arrangement can serve for washing the bicarbonate and the lime-mud.

In Germany and Austria Messrs. Honigmann, Gerstenhöfer, and Bolley were chiefly active in erecting works for the ammoniacal soda-manufacture. All of these have been stopped again, except Honigmann's own small works near Aachen; but quite recently new plants on different systems have been erected in a few places.

Honigmann's process is sketched by Landolt in Hofmann's Bericht, 1875, vol. i. p. 452; other notes are found in Post's Zeitschr. f. d. chem. Grossgew. i. p. 105. His apparatus is very different from that of Solvay. The operations are carried out in large cylinders of boiler-plate, six of which, 10 to 13 feet high and wide, suffice for a make of 5 tons per diem. The $CO_2$ gas is forced through ammoniacal brine contained in three vessels, through a depth of altogether 20 to 23 feet, over a surface of about 100 square feet, at a temperature of from 25° to 35° C. The liquor, containing about 12·5 per cent. $NH_4Cl$ and 2·5 to 3 per cent. $(NH_4)_2CO_3$, is distilled with lime by exhaust-steam only. It is separated from the bicarbonate by centrifugal machines. The latter yields ash of 97·5 to 98·5 per cent. $Na_2CO_3$. The steam-boilers for 5 tons ash per diem [this is a maximum !] have a heating-surface of nearly 1000 square feet. For 5 tons soda ash 12½ tons salt, 7¼ tons coals, 1¾ ton coke, 5 tons limestone, 5 cwt. ammonium chloride (loss), ½ cwt. sulphuric acid, and 11 men at day, 8 at night, along with 10 men for yard-work, are required. The author, from his own inspection, must confirm the above statements as far as the apparatus is concerned, which looks extremely simple and cheap compared with that of Solvay. The brine, originally 36° Tw., is saturated in simple vessels with ammonia so as to correspond to 18 per cent. $NH_4Cl$ upon 100 $Na_2CO_3$; in the same vessels the salt is dissolved from the first, and the sediment taken out. One cylinder settles while the other one is being saturated. The ammonia-still is a simple cylinder, 12 to 15

feet wide and 6 feet high, heated by the exhaust-steam of the blowing-engines. In this still, as well as in the dissolvers for salt and ammonia, there is always a certain partial vacuum maintained by an air-pump, so that no $NH_3$ can escape outside. The precipitation with $CO_2$ takes place in two connected vessels about 10 feet high and wide, supplied by the gas from the lime-kiln, containing at the best 30 per cent., and that from the calcining furnace, containing 20 per cent. $CO_2$. The bicarbonate is drained in centrifugal machines, washed in the same till it is strong enough, and calcined in an open drier. The apparatus are always kept whitewashed, because they are very liable to rust.

According to Honigmann's advertisements, the plant for turning out 5 tons of strong soda ash per diem costs £4500; for 100 parts of soda ash he requires, according to different advertisements (*a, b, c*) and to verbal statements made to the author (*d*)*:—

| | *a.* 90 p. c. ash. | *b.* 95 p. c. | *c.* 98 p. c. | *d.* 98 p. c. ash. |
|---|---|---|---|---|
| Rock-salt | 200 | 190 | 175 | 250 |
| Coal | 200 | 175 | 150 | 250 |
| Coke | ...... | ...... | ...... | 45 |
| Limestone | 150 | 140 | 130 | 140 |
| Sulphuric acid, 106° Tw. | 10 | 8 | 6 | ...... |
| Sal-ammoniac | 5 | 4 | 3 | 5 |
| Workmen | ...... | 20 | ...... | ...... |

Although Honigmann guaranteed the figures sub *b* to be realized directly after starting, all the works erected on his plan (except his own) have stopped. So has a works erected at Wyhlen near Basel by L. Bolley, the plant of which has not been publicly described; but it is known that a pressure of 4 or 5 atmospheres, and large absorbers 10 feet wide, were employed there.

A circular of Messrs. Wegelin and Hübner, of Halle, in conjunction with Mr. Pollacsek, dated Feb. 1878, states the cost of plant for a daily make of 10 tons ash of 98 per cent. $Na_2CO_3$ at £8627, to which £2250 for buildings and masonry must be added. This would be much less than Solvay's costs, but had not yet passed through the ordeal of practical experience. The circular states the materials &c. required for 10 tons 98-per-cent. soda as

* The author cannot in any way explain the divergencies of these statements from one another, and from that on the preceding page.

follows :—

| | In Central Germany. | | | | | In England. | |
|---|---|---|---|---|---|---|---|
| | cwt. | At per ton. s. | Total. s. | At per ton. s. | Total. s. | At per ton. s. d. | Total. s. d. |
| Salt from brine | 360 | 9 | 162 | ... | ... | ... | ... |
| Rock-salt | 360 | ... | ... | 16 | 288 | 10 7 | 190 9 |
| Coal | 380 | 12 | 228 | ... | 228 | 6 0 | 114 0 |
| Limestone | 200 | 8 | 80 | ... | 80 | 5 0 | 50 0 |
| Ammonia salt | 6 | 500 | 150 | ... | 150 | 500 0 | 150 0 |
| Workmen (40) | ... | 2 | 80 | 2 | 80 | 5 0 | 225 0 |
| Management | 2 | 5 | 10 | 5 | 10 | 8 0 | 16 0 |
| | | | 710 | | 836 | | 745 9 |
| Packages and sundries | ... | ... | 170 | ... | 170 | ... | 170 0 |
| 10 p. c. amortization and 5 p. c. interest on capital | ... | ... | 100 | ... | 100 | ... | 100 0 |
| | | | 980 = £49. | | 1106 = £55 6s | | 1015 9 = £50 15s. 9d. |

This calculation is highly coloured, with the intention of showing that Germany can produce ammonia-soda as cheaply as England, or even more so. This endeavour has given rise to such ridiculous mistakes as that "England can only work with rock-salt," although in reality *all* ammonia-soda in England is made from brine, and all other soda ash indirectly from the same, through common salt. Several factories on this latter system have been quite recently erected in France; it is too early as yet to judge of their success.

A patent taken out by J. Young (Sept. 28, 1872), which has never been carried out practically, describes an apparatus for the ammoniacal manufacture of soda, represented in figs. 27 to 29: fig. 27 is a front elevation; fig. 28, a plan; fig. 29, a back elevation. It consists of three cylindrical, air-tight, iron vessels

A, B, and C, carried by journals D, revolving in bearings E fixed in the framing F. Beneath each of the cylinders a fire-grate, G, is situated; and at one end of each vessel a bevel wheel, H, is

Fig. 27.

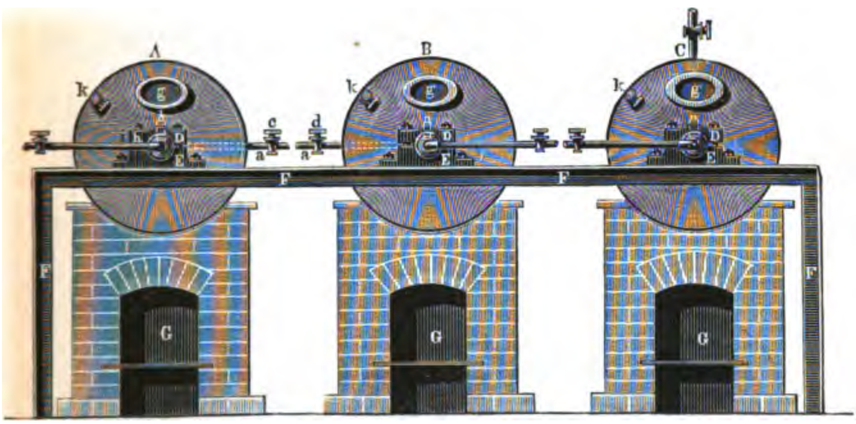
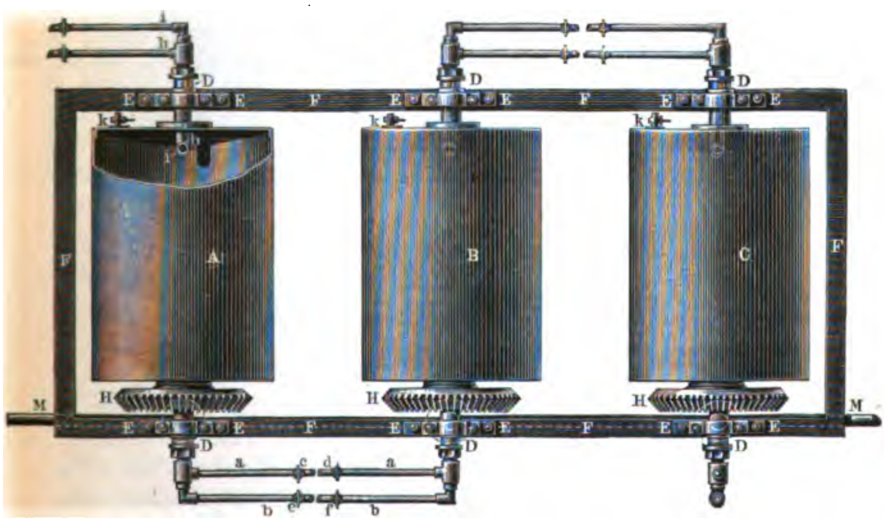


Fig. 28.

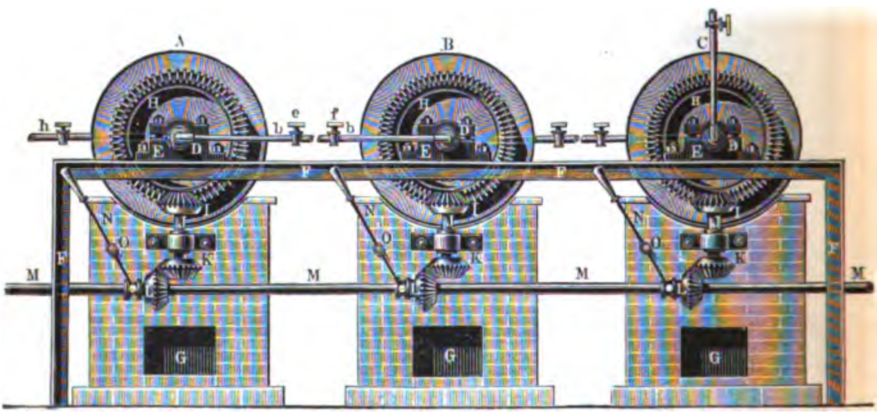


attached. The wheels H are in gear with bevel pinions, I, carried on short vertical shafts, J, each of which has at its lower end

another bevel pinion, K, in gear with similar bevel pinions, L, on the horizontal shaft M. The pinions L are provided with levers, N, movable on studs, O, by which the pinions L can be thrown in and out of gear with the pinions K when required. Any two of the cylinders A, B, C communicate by pipes passing through the hollow journals D of any other of the vessels. We will assume that the vessels A and B are in communication by the pipes *a* and *b* provided with stop-cocks *c, d, e,* and *f*.

In commencing the operation the door *g* in the end of the vessel A is removed and a solution of salt (1 part in 3 parts of water) run in; its surface must be well below the ends of the pipes *h* and *i*,

Fig. 29.



which may be turned upward inside the vessel, as shown in fig. 28. The door *g* is closed air-tight; through *h* ammonia gas, in the proportion of 35 $NH_3$ to 100 NaCl, is admitted; through the pipe *i*, passing through and ending above the pipe *h*, carbonic acid is introduced, obtained by heating sodium bicarbonate or from calcium carbonate heated to redness in a retort with steam passed through it. By causing the vessel A to revolve, fresh surfaces are constantly exposed; this may be assisted by perforated disks or a series of arms inside the vessel. When sodium bicarbonate begins to be precipitated, the temperature is kept at 50° C. The admission of $CO_2$ is continued until absorption ceases. During this time the unabsorbed gas passes over through the pipes *a, b*

into the vessel B, in order to act upon a fresh charge of salt water and ammonia. In B less than 3 water to 1 salt is contained, viz. by as much as passes over from the ammonia-still and in the subsequent heating of the bicarbonate solution in A. After the absorption is complete, the rotation of A is stopped, the bicarbonate allowed to settle, the solution of ammonium chloride discharged into the ammonia-still through the cock *k* and a pipe which is temporarily affixed; the remaining salt may be washed with water or a solution of common salt, and the washings also run into the still. Water is then added to the bicarbonate, and the vessel A gradually heated to the boiling-point, 105° C. The boiling may be effected by superheated steam instead of an open fire. Thus any ammonia still present and half the carbonic acid are expelled; they first pass through a refrigerator, and then into the vessel B; the solution remaining in A is worked either for crystal soda or soda ash.

Hugo Müller (of Düsseldorf), on Dec. 28, 1874, patented for the ammoniacal soda-manufacture an apparatus which can be used also in other cases where liquids have to be brought into intimate contact with gases. Similarly to Young he employs several apparatus connected together, shaped like funnels at the bottom, and semicircular at the top; a centrifugal pump moves the liquid from the lower into the higher compartment, pours it over a trough with perforated bottom and a filtering cloth above this, and thus divides it minutely, whilst the solid particles remain behind in the trough, which can be easily taken out.

Gerlach (Dingl. Journ. ccxxiii. p. 82) combines the working-up of ammoniacal gas-liquor with the manufacture of soda. The gas-liquor is distilled; in the distillate, chiefly consisting of ammonium carbonate, common salt is dissolved; and $CO_2$ is passed into it as long as any sodium bicarbonate is precipitated. The liquor now contains some ammonium carbonate (which is distilled off), and ammonium chloride and undecomposed sodium chloride (which must be separated in a suitable manner).

The only "novelty" is the utilization of the ammonium chloride by sale, instead of by recovering the $NH_3$; but this had been proposed several times previously, and this just confines the employment of the process to the narrowest possible limits. Besides, Gerlach proposes treating ammonium carbonate with sodium sulphate; but this will not contribute to economy, as ammonium

sulphate is much cheaper than chloride. Ammonium nitrate is to be made in a similar manner. The original also contains proposals for separating the chlorides and sulphates of sodium and ammonium by concentrating and crystallizing.

Wallace and Claus, on Jan. 20 and July 25, 1877 (Chem. News, xxxviii. p. 263) patented a process intended to combine the purification of coal-gas with the ammoniacal manufacture of soda. The coal-gas is to be purified entirely with ammonia (instead of with lime or iron oxide), which is applied in a series of scrubbers constructed in a peculiar way and fitted with angle-iron bars lying crosswise. The $H_2S$ is gradually driven out by $CO_2$, so that chiefly ammonium sulphide is found in the scrubbers away from, and ammonium carbonate in those near to the retorts; the former even contain an excess of $CO_2$, and $H_2S$ only in the free state. In this liquor common salt is dissolved and pure $CO_2$ (obtained by decomposing sodium carbonate) passed into it. The precipitate (consisting, as usual, of sodium bicarbonate) is heated in a closed vessel, the $CO_2$ being collected in a gas-holder and applied as above stated. The solution, containing ammonium chloride, some sodium chloride, and ammonium bicarbonate and sulphide in excess, is heated to drive off the latter, and then run upon heated hydrate of lime: all the $NH_3$ is thus liberated, and is again admitted into coal-gas, where it starts the purifying process anew. The ammonia contained in the gas is available for other purposes; it is found as ammonium sulphide in the last scrubbers, and suffices for absorbing three fourths of all the $H_2S$ contained in the gas. In this process there is a saving, as against the ordinary ammoniacal soda process, of all the carbonic acid and of the ammonia lost.

Calculated from the $CO_2$ usually contained in coal-gas, each ton of coal employed in the gas-works ought to yield from 70 to 84 lb. of purest soda ash; the London gas-works alone would produce about 1100 or 1200 tons per week; and the large provincial towns would make this up to 4000 tons per week.

The ammonium sulphide is partly employed for purifying coal-gas from carbon disulphide; but for the most part it is decomposed by sulphuric or hydrochloric acid, and the (almost pure) sulphuretted hydrogen utilized as described in Vol. II. p. 649. Or the solution of ammonium sulphide is concentrated and treated with sulphurous acid; the ammonium hyposulphite thus formed is decomposed by sulphuric acid, and the sulphurous acid now liberated utilized for the purification of coal-gas from sulphuretted

hydrogen, in which case sulphur is precipitated and collected. This process has not been tried yet. Evidently it has considerable difficulties to surmount; but how far these are fatal, only the experiment could show. The chief question would be, whether the purification of the gas in this way is really efficient, and whether the resulting liquor is not too impure (tarry) to be applied for the direct decomposition of salt.

Unger (German patent, No. 2295, Oct. 25, 1877; Dingler's Journal, ccxxxi. p. 436) saturates the ammoniacal brine first with dilute lime-kiln carbonic acid in an upright iron cylinder with a jacket for cooling-water, and a vertical quickly revolving shaft carrying disks, by which the liquid running down is violently splashed about. The fire-gases in the first apparatus travel downwards, in the second one upwards, so that the $NH_3$ carried away can be washed out by NaCl solution. The solution of ammonium monocarbonate and common salt is now saturated in other cylinders with pure $CO_2$ from decomposing the $NaHCO_3$ under pressure. For more easily absorbing the $CO_2$ there are narrow spirals fixed in the cylinders, which distribute the $CO_2$ and by their mobility prevent the adhesion of crusts to them. The saturation of brine with $NH_3$ takes place in a cylinder fitted with small upright tubes, each tube being a little to one side of the pipes below. In similar apparatus the last remnant of $NH_3$ is washed out of the escaping pure $CO_2$ and the fire-gases.

E. Mond has patented the following improvements (Dec. 4, 1874). In order to purify the brine, to each 1000 gallons of it ¾ cwt. of soda ash and 20 lb. of lime are to be added and the clear liquor drawn off (comp. pp. 8 & 35). Iron is removed by introducing into the ammoniacal brine the products of the distillation of gas-liquor, containing ammonium sulphide.

Verzijl obtained a Belgian patent (Dec. 30, 1876) for compressing the carbonic acid to the density of 3 atmospheres, in order to produce a lowering of the temperature by the sudden expansion of the gas in forcing it through the ammoniacal brine. This principle is precisely the same as that employed by Solvay.

Boulouvard took out some French patents (May 6, 1872; Oct. 7, 1877) on this matter, containing "improvements" in apparatus. The only "novelty" is that he does not pass $NH_3$ into brine, but first makes liquor ammoniæ containing 9¼ to 9½ per cent. $NH_3$, and dissolves salt in it. His $CO_2$ is made by heating limestone in retorts in superheated steam. His process is being introduced

(1878) into the Usine du Griffon at Sorgues (Vaucluse); with what result remains to be seen.

A special arrangement of plant for the ammoniacal soda-process has been patented in Germany by Count de Montblanc and Le Gaulard (No. 8498, May 20, 1879).

Bernard patented in France (Oct. 6, 1877) the employment of substitution ammonias, especially methylamine, in the place of ordinary $NH_3$ in this manufacture. It is very unlikely that these amines will ever be employed in the manufacture of soda. For that of potassium carbonate their employment may possibly be more indicated; it has been patented for that purpose in Germany by the Croix Company near Lille (No. 5786, Oct. 6, 1878).

Scherbascheff (Wagner's Jahresb. 1876, p. 338) patented, in several countries, the following process. By dissolving common salt and ammonium carbonate in the same vessel at from 60° to 70° C., he professes to obtain almost insoluble [?] monohydrated $Na_2CO_3$ and a solution of $NH_4Cl$. At a higher temperature than the above the ammonium carbonate would be dissociated into $CO_2$ and $NH_3$ and the reaction inverted. For actual practice [?] he half fills two tubs with water or brine. In one of these several baskets with salt in lumps are suspended, and the whole heated up to 60° C.; then other baskets are suspended with ammonium carbonate. The reaction at once sets in: $Na_2CO_3 + H_2O$ is precipitated as a crystalline powder; and $NH_4Cl$ remains in solution. Moreover $NH_3$ and $CO_2$ are given off, which are carried off by a pipe in the cover of the vessel into the liquor of the second tub. The operation is finished when the hydrometer shows the liquor to be saturated with $NH_4Cl$; then the baskets with salt and ammonium carbonate are taken out and hung in the second tub. The first tub is still heated to 60° or 70° for some time, in order to precipitate all the soda. The solution of ammonium chloride is run off for crystallization, and the soda taken out of the tub. After centrifuging, washing with boiling solution of soda, and drying, it is ready for sale. The crystallized $NH_4Cl$ is worked up into ammonium carbonate in the well-known way; the mother liquor is employed in the tubs as above.

[This process is wrong in principle, and the details evidently worked out by an unpractised hand.]

Thowald Schmidt, of Aalborg in Denmark (Chem. News. xxxiv. p. 201, xxxvii. p. 56), adds to the concentrated solution of NaCl and $CaCl_2$, obtained in recovering the $NH_3$, a concentrated solu-

tion of kelp. The potassium, sodium, and magnesium sulphates in the latter are hereby decomposed, and $CaSO_4$ and $Mg(OH)_2$ precipitated in a form suitable for use as "pearl hardening" in paper-making. The last traces of the sulphates are removed by barium chloride. To the clear solution lead nitrate is added till all the iodine has been thrown down as $Pb\,I_2$, which is filtered off and worked up for iodine. The filtrate is heated, lime and magnesia precipitated by soda, the KCl converted into $KNO_3$ by $NaNO_3$, and the saltpetre removed by crystallization. There remains a solution of NaCl with traces of KCl and of $NH_3$ (from the last operation); this is again submitted to the ordinary ammoniacal soda-process. This process can at best only pay in very exceptional circumstances, where salt is very dear; but then the ammonia process is at any rate out of place here. Recently (Chem. News, xxxviii. p. 203) Schmidt has given a pretty detailed description (somewhat obscure, owing to the want of diagrams) of the apparatus used in the ammoniacal soda-manufacture at Aalborg (now stopped). According to his statements, there are needed daily for 10 tons of soda:—salt, 16 to 17 tons; coal, 17 to 18 tons; coke, 3 tons; limestone, 12 tons; sulphuric acid of 106° Tw., 2 cwt.; ammonia salt, from 4 to 6 cwt.; and 45 men.

The *theory* of the ammoniacal soda-process has been repeatedly treated of. We have already seen that Heeren and Schlösing found that the conversion of NaCl into $NaHCO_3$ stops at $\frac{2}{3}$ or $\frac{4}{5}$ of the whole. Al. Bauer (Deutsche chem. Ges. Ber. vii. p. 272) shows that this incompleteness of the decomposition is not merely due to the solubility of sodium bicarbonate, as was previously believed, but to the fact that the carbonates of sodium may mutually decompose with ammonium chloride into ammonium carbonate and sodium chloride, and that under very varying circumstances:—*e.g.* on the spontaneous evaporation of a solution of $NaHCO_3$ and $NH_4Cl$ at from 8° to 15° C.; also on their spontaneous evaporation in a current of $CO_2$; and also with not fully concentrated solutions, saturated with $CO_2$, when exposed to a temperature of −15° C. The following process then takes place:—

$$CO(ONa)(OH) + NH_4Cl = CO(ONH_4)(OH) + NaCl.$$

Even at a higher temperature this decomposition is still noticeable. Günsberg (*ib.* vii. p. 644) noticed the same inversion of the reactions of the ammoniacal soda-process in all his experiments;

he takes it as a matter of course, considering the volatility of ammonium carbonate and the solubility at different temperatures of the salts in question. That portion of $NaHCO_3$ which remains dissolved in the $NH_4Cl$ solution will be always lost; and care will have to be taken that from the very first a saturated solution of $NH_4Cl$ is obtained which at a certain pressure contains the minimum quantity of sodium compounds. He found that at ordinary temperature and pressure 100 parts of a $NH_4Cl$ solution, saturated at 17° C., contain dissolved 25·89 parts $NH_4Cl$ and 5·742 parts $NaHCO_3$. This will be the case when at the ordinary temperature 58·5 parts of NaCl are treated with 180 parts of a liquor containing 10·396 per cent. $NH_3$.

According to Honigmann's experiments (quoted by Landolt *l.c.*),

I. A solution containing per litre

265 grams NaCl (=104 grams Na) and
77 " $NH_3$ (=1 eq. NaCl : 1 eq. $NH_3$),

after being saturated with $CO_2$ at 15° C. under ordinary pressure, yielded:—

(*a*) a precipitate consisting of

251 grams $NaHCO_3$ (=69 grams Na) and
33 " $(NH_4)HCO_3$ (= 7 " $NH_3$);

(*b*) a solution containing

35 grams Na as NaCl or $NaHCO_3$, and
70 " $NH_3$ " $NH_4Cl$ and $(NH_4)HCO_3$.

II. On passing $CO_2$ into a solution containing per litre 331 grams NaCl (=130 Na) and 70·8 $NH_3$ (=4 NaCl : $3NH_3$) there were obtained:—

(*a*) a precipitate of

286·2 grams $NaHCO_3$ (=78 Na) and
15 " $(NH_4)HCO_3$ (=3·2 $NH_3$);

(*b*) a solution of

52 grams Na as NaCl or $NaHCO_3$ and
67·5 " $NH_3$ " $NH_4Cl$ and $(NH_4)HCO_3$.

Accordingly, there have been converted into bicarbonate, of each 100 parts Na employed as NaCl,

In exp. I. ($NaCl+NH_3$) 66 parts,
" II. ($4NaCl+3NH_3$) 60 "

Calculated for ammonia, there were precipitated as bicarbonate, upon 100 parts of $NH_3$,

In exp. I. ($NaCl+NH_3$) 90 parts Na,
" II. ($4NaCl+3NH_3$) 110 " "

In experiment II. much less ammonium bicarbonate was precipitated along with the sodium bicarbonate than in I. [These experiments would seem to prove that the best proportion is 4 molecules NaCl to 3 molecules $NH_3$; but this is at variance with Günsburg, who requires 18·72 $NH_3$ for 58·5 NaCl, *i. e.* much more than an equivalent.]

A modification of the ammonia process, the *alcohol ammonia process*, has been patented in several countries by H. de Grousilliers, of Berlin, and further worked out in conjunction with W. Siemens (Hofmann's Bericht, 1875, i. p. 454; French patent of March 16, 1875). It is founded upon the fact that alcohol of sp. gr. 0·90 does not dissolve the carbonates and bicarbonates of sodium and potassium, but absorbs very much $NH_3$ and $CO_2$; the chlorides of ammonium, potassium, and sodium are soluble to some extent in the same. If they meet with an alcoholic solution of $NH_3$ and $CO_2$, an alkaline carbonate is precipitated, and the more completely the stronger the spirit. The precipitate obtained with NaCl is essentially $NaHCO_3$, even with a large excess of $NH_3$. Experiments made in Hofmann's laboratory seemed to show that this process was superior to the ordinary ammonia process [? The detailed statements prove yields of 58·18, 66·19, 72·26 per cent. of the theoretical one].

The practical success of this process evidently depended upon avoiding to the utmost any loss of alcohol. This was not at first done to a sufficient extent; but a continuously working apparatus, constructed by Mr. Siemens, seemed to solve the problem. Into the cylindrical apparatus there were introduced at the same time ground rock-salt, spirit of wine of 35 per cent., gaseous $NH_3$, and $CO_2$. Mechanical agitation assisted the decomposition; and the lower specific gravity of the sodium bicarbonate formed was made

F 2

use of to separate it from the unchanged rock-salt. The spirit, charged with $NH_4Cl$, entered a continuously acting regenerator, where it was treated with lime, and again yielded alcohol and $NH_3$. The operations all taking place in air-tight vessels, the loss of alcohol was not to exceed $\frac{1}{2}$ per cent.; and there was also to be much less loss of $NH_3$ than in Solvay's process. The bicarbonate was both pressed and washed in a continuously acting press, conveyed to a heating-apparatus, and turned out as a finished alkali. Later on (Wagner's Jahresb. 1876, p. 337) the inventor stated the loss of $NH_3$ at only $\frac{1}{100}$ per cent., that of spirit at $\frac{1}{8}$ per cent. This process (which did not suffer from any modesty of statement respecting it) was actually introduced into Messrs. Kunheim's works at Berlin; but all that has been made known about it is, that it entirely failed there, and that both Kunheim and Siemens have withdrawn from it. The inventor himself has allowed the patent to lapse.

The question whether the ammoniacal soda-process is destined to displace Leblanc's process entirely or for the most part has been discussed by every alkali-maker, and several times publicly. To the established success of Solvay and the English works built upon his plan is opposed the failure of well-nigh every other attempt in this direction (at any rate up to the date of writing this). The contradiction is probably explained by the fact already stated, viz. that this process is much less a chemist's than an engineer's business, and that consequently one apparatus may work very well, another very badly. But supposing that everywhere proper apparatus were constructed and success similar to Solvay's obtained, what would be the state of matters then? Would the manufacture of soda ash by Leblanc's process have to cease? It seems certain that at present the soda made by Solvay himself is cheaper than soda of equal strength made by Leblanc's process in the same place. But in England it would appear that the ammonia ash can only compete with the ordinary ash owing to its superior quality, which causes it to be saleable at a considerably higher price for purposes where purity is a first object; where the latter is not of such importance, the ordinary alkali securely keeps its place in this country as yet. Moreover, at many of the large works the manufacture of caustic, which cannot be very well combined with the ammonia-process, is far too important to be given up lightly. Crystal soda, too, is made more

easily by the Leblanc process, at any rate now that the cyanide and sulphide can be almost entirely removed from the tank-liquors.

The case is different in Germany and France, where undoubtedly at present Solvay's soda is cheaper than that made by the Leblanc process. In those countries the ammonia process will probably spread a good deal more, especially under favourable local circumstances, *e. g.* in the presence of strong brine-springs along with coal-beds. But it seems doubtful whether it will be adopted in many other cases, considering the inevitable rise in the price of ammonia, the non-production of hydrochloric acid, and, to a minor extent, the bulkier state of the ammonia-soda. The latter will probably be got over in the end; but there is no prospect as yet of *cheaply* making HCl from $CaCl_2$, or even from $MgCl_2$. So far as we can see, soda and hydrochloric acid *together* will always cost more with the ammonia process than with the Leblanc process; hence, wherever hydrochloric acid is valuable (and this is the case in most continental works) the ammonia process will be the exception, the Leblanc process the rule. This may be all the more safely predicted since during the last few years the German alkali-makers, stimulated by the sharp competition of Solvay's ash, have learned to turn out their ash *fully* equal in colour and strength to the best ammonia ash, to which it is even superior in regard to density.

A very general extension of the former process would be prevented by the fact that the price of ammonia would rise too much and would become prohibitory to that system. As it is, the price of ammonium salts has risen enormously during the last ten years, owing to the continually increasing demands of agriculture; and it cannot be said that nothing but an impetus such as that given by the new soda process was required for finding out new sources of those salts. Even on the most favourable assumption, the loss in the ammoniacal soda-manufacture averages 5 parts of ammonium sulphate per cent. of the soda; but if only half of all the soda now made were manufactured at such a loss of ammonia, none would remain for other purposes—or, rather, that kind of manufacture must have been stopped long since, because ammonia would have become too dear. Solvay remarks, in his pamphlet of 1878, that agriculture would have to give up ammonia entirely, and take nitrate of soda instead But it is very doubtful whether

this is such a simple matter; otherwise nitrate of soda would not be so cheap and ammonia salts so dear now*. If (what cannot be pronounced upon with certainty as yet) illuminating-gas should be replaced to any considerable extent by the electric light, this will at once cause another large increase in the price of ammonia. According to Roscoe (Chem. News, xxxix. p. 107) the total quantity of ammonia obtainable from the ammonia-water of all the gas-works in Britain amounts to 9000 tons per annum.

Among the many attempts to open up new sources of ammonia we shall only mention the most recent. Maxwell Lyte patented, on Feb. 15th and May 31st, 1875, in France, the action of a current of steam along with nitrogen upon certain alloys or other compounds of the metals of the alkalies or alkaline earths or zinc, by which hydrogen becomes free and in the nascent state combines with nitrogen to form ammonia. He employs alloys of Na, K, or Zn with Sb, Bi, As, or Sn, produced by a simultaneous reduction of the metals.

Solvay himself patented on March 27th, 1875, in France, the following process:—Ammonium chloride is formed when a current of steam, HCl, and air or N is passed through a coke or charcoal fire. Under these conditions (in the presence of a base at a high temperature) cyanogen must be formed; and under the influence of steam and HCl this passes over into $NH_4Cl$. The HCl can be replaced by a decomposable chloride, with which the red-hot coke or charcoal is impregnated; this chloride in contact with steam yields both the requisite base and acid. The fuel is charged into a cupola, impregnated with chloride of barium, calcium, magnesium, or even of potassium or sodium, along with alumina and silica; but it is better to mix the fuel with limestone soaked in the chloride. Draught is produced by artificial means. (This principle is not novel, having been put forward by Wagner in his Jahresbericht, 1857, p. 122.)

Moerman-Laubuhr, on May 13, 1875, patented the employment of blast-furnaces with two openings in the top, one of which serves for introducing the charge. This consists of a mixture of one or two parts coke or charcoal with one part alkaline salt (serving as a basis for the formation of cyanides), powdered, moulded into bricks, and dried. The air is deprived of its oxygen by red-hot

* This was written before the war in South America had caused a considerable rise in the price of nitre.

coke; and the resulting mixture of $CO_2$ and N converts the bricks into cyanide, which collects at the bottom and is tapped twice a day. [This process for producing cyanides is very old; and it is well known that it has been given up long since, after many costly trials made both in England and France.] The cyanide is to be transformed into ammonia by any of the four following processes:—1. Dissolving and boiling for some time, the $NH_3$ going away as gas. 2. Fusing with manganese peroxide, dissolving the cyanate formed, and boiling with water; ammonium carbonate escapes and is absorbed in a mixture of ground gypsum and water, by which ammonium sulphate is formed. 3. By igniting the cyanide or cyanate with coal in a current of air mixed with steam. 4. By decomposing with concentrated acid; but in this case much prussic acid is liberated, and this process consequently cannot be recommended [neither can the others].

Grouven (German patent, No. 2709, 1878) distils moor-peat, and passes the gases over a "contact-mass" consisting of peat, chalk, and clay, which is to increase the yield of ammonia.

Legrand and Dubernard (French patent, Dec. 27, 1876; Bull. Soc. Chem. xxx. p. 480) produce ammonia by the action of steam upon the potassium cyanide contained in the crude potash made from the "vinasses" of beet-sugar-works and from wool-sweat. This material furnishes 1 to 4 per cent. of ammonium sulphate; 5 cwt. of it require only ½ hour's treatment and 5 lb. steam.

Rickmann (English patent, Aug. 1878) believes it feasible to manufacture ammonia by passing air and steam over coke or spongy iron heated to about 550° C. The steam decomposes in contact with the red-hot coke; and the liberated hydrogen is supposed to combine with atmospheric nitrogen to form ammonia.

The ingenious process of C. Vincent (described by Prof. Roscoe, Chem. News, xxxix. p. 107), for the better utilization of beet-root "vinasse," certainly produces ammonia from a hitherto neglected source; but this can hardly ever become a very important one, and the ammonia thus obtained will probably have to be restored to the soil again as manure.

Some hopes have been entertained of obtaining the large quantities of ammonia which are given off in the combustion of coal generally. This, however, would seem to be hardly more practicable than, for instance, recovering the gold, silver, iron, &c. lost by wear and tear. Any more definite hopes in that direction

could only be connected with the coking-process; but hitherto nearly all endeavours to condense ammonia-water and tar in that process have ended in failure, the quality of the principal product, the coke itself, being found to suffer considerably under that treatment.

According to the Inspector's Report for 1877–78, p. 48, there were destroyed in 1876, in England, 36,000 tons $NH_3$ (=139,764 tons sulphate of ammonia) in only manufacturing coke for iron from 15 millions of tons of coal. In the same place will be found an exhaustive report of the coking-process as carried out at Bességes in France, according to Knab's patent, where both ammonia and tar are saved. The result is stated to be extremely favourable—the theoretical yield of coke, excellent quality of the same, and a gain for each oven producing 390 tons coke per annum, of 10,600 kilog. tar and 2132 kilog. sulphate of ammonia, leaving a profit of 0·048 franc per kilog. upon the former and of 0·25 franc upon the latter. (Against this profit should be set off the interest and amortization on the considerably greater outlay for plant required by this process.)

In the same place, p. 65, there is a letter from Mr. Lawes, according to which 24 per cent. sulphate of ammonia at £18 per ton corresponds in value to nitrate of soda at £14: the latter is generally cheaper than that, and for most purposes better than sulphate of ammonia. Still of the latter 100,000 tons could be sold without any very serious reduction in price.

# CHAPTER XVII.

## THE MANUFACTURE OF SODA FROM CRYOLITE*.

### *Historical.*

THE mineral *cryolite* was found for the first time at Ivitût, in South Greenland, by a Danish whaler, who brought a piece of it to Copenhagen, without stating where it came from. It was first described by Schumacher, in 1795, and analyzed by Abidjaard, more correctly by Klaproth, who proved it to contain soda—the first time that this alkali had been found in the mineral kingdom otherwise than as common salt. Further analyses by Vauquelin, Berzelius, and Deville completely established the composition of the mineral. The original occurrence of the mineral in Greenland was discovered by Giesecke after long seeking (1806–1813). Up to 1849 it was only found in scientific collections; but in 1849 Professor Julius Thomsen at Copenhagen proved cryolite to be easily decomposable by lime both in the dry and in the wet way, and showed its applicability to the manufacture of soda. In 1854 he obtained an exclusive right (till 1884) of mining for cryolite and working it up in Denmark for soda and alumina; this right was afterwards sold to a company. The first small factory was built in 1857, at Copenhagen; the first large one, still existing, at

* The most complete and recent description of this industry is that by Benzon, in Hofmann's 'Bericht,' 1875, i. p. 660. Other, but partly antiquated, sources which have been consulted are:—Wagner's 'Regesten,' p. 57, and 'Jahresberichte' for 1862 and 1868; Knapp's 'Chemische Technologie,' 3rd ed. i. 2, p. 471; Wurtz, 'Dictionnaire de Chimie,' ii. p. 1557; E. Kopp, 'Schweizer Ausstellungs-Bericht,' 1873, iii. p. 20; Goldschmiedt, 'Oesterr. Bericht,' 1877, vii. p. 12; the English patent-specifications, and the author's personal observations at the former cryolite-soda works at Golschmieden near Breslau.

Oeresund near Copenhagen. In 1861 and later on, factories were erected at Harburg, Mannheim, Prague, Goldschmieden near Breslau, and Warsaw. All the latter works have had to discontinue the use of cryolite, since the Pennsylvania Salt-manufacturing Company at Natrona near Pittsburg, in 1865, obtained a right to two thirds of all the cryolite produced (*in maximo* 6000 tons per annum) up to 1884. In 1855 H. Rose proposed this mineral for the manufacture of aluminium.

On the whole, from 1856 (when first whole cargoes were shipped) to 1873, 68,000 tons of cryolite were got; since 1865, about 6000 or 7000 tons per annum.

All cryolite comes from Ivitût, from a valley on the south side of Arsuk Bay, where summer lasts three months. Some of the mineral is found below low-water mark, but in a more impure state. On the mainland there is a bed of 30,000 square feet of white cryolite lying above impure mineral. Any mineral containing more than 20 per cent. impurities is rejected. The purest is 10 feet below the surface; below 15 feet it becomes very dark, and at last almost black; but on igniting the latter, it also becomes white. The impurities are galena, copper-pyrites, spathic iron-ore, fluor-spar, and lime-spar; the surface is covered with clay and sand. The working takes place chiefly from April to the end of December, and to a certain extent even during the remaining months.

Pure cryolite is a semitransparent, snow-white, glassy mineral; in the impure state it is yellow or reddish. Its specific gravity is 2·953, its hardness 2·5 to 3. The crystals are very indistinct; but the mass has a good cleavage along the faces of a square or oblong prism. It is easily fusible, and in a glass tube shows the reaction of fluorine. It is incompletely soluble in hydrochloric acid, completely in concentrated sulphuric acid, and is also decomposed by lime. Its chemical formula is $Al_2F_6,6NaF$; in the pure state it would contain :—

| | | | | |
|---|---|---|---|---|
| Aluminium | 13·07, | corresponding to | alumina ............ | 24·54 |
| Sodium | 33·35 | ,, | soda ($Na_2O$) ...... | 44·79 |
| Fluorine | 53·58 | ,, | hydrofluoric acid.. | 56·44 |
| | 100·00 | | | |

For *working up cryolite* into soda and alumina many processes

have been proposed, only one of which is carried out in practice, viz. the dry treatment with calcium carbonate: this will be described more fully now; and the others will be briefly mentioned afterwards.

The present process was discovered by Thomsen in 1850; he is undoubtedly the originator of the entire industry (Dingler's Journal, clxvi. p. 441); and all other works have been laid out after his plan. The process is founded upon the fact that, on igniting cryolite with calcium carbonate, carbonic acid escapes, and calcium fluoride and sodium aluminate remain behind:

$$Al_2F_6, 6\,NaF + 6\,CaCO_3 = Al_2O_3, 3\,Na_2O + 6\,CaF_2 + 6\,CO_2.$$

Both the cryolite and chalk are finely ground by edge-rollers. To 100 cryolite 150 chalk is employed, instead of 127 as required by the formula; the excess of chalk makes the mass more porous and less fusible. In spite of the finest grinding and mixing of the materials, a portion of the cryolite inevitably becomes surrounded by the sodium aluminate formed, by which its decomposition is prevented. Some years ago Hagemann and Jörgensen succeeded in avoiding this drawback by adding to the mixture some of the impure calcium fluoride obtained in the process itself. This causes more consumption of fuel, and requires twice the number of furnaces, but increases the yield from 12 or 13 per cent. alumina and 60 alkali to 18 per cent. alumina and 68 or 70 alkali.

A proper temperature is of great importance for this process. The decomposition begins below a red heat; but in practice the latter must be attained in order to complete it. The melting-point of the mixture is not very much higher; so that there is only a short range between the two. The mass, being a bad conductor of heat, must be in a thin layer. If it gets to the melting-point, much cryolite is protected from decomposition, and the lumps formed are very difficult to lixiviate. Hence ordinary reverberatory furnaces are not applicable, because in these the heat is too unequal, and one portion of the mixture would be fluxed before the other was decomposed. [Undoubtedly mechanical furnaces like those employed in black-ash and sulphate making and carbonating, would do the work most completely.] The furnace constructed by Thomsen, which avoids the above-mentioned drawback, has the shape shown in figs. 30 to 33. The furnace-bed, C, is made of fireclay lumps 18 inches square and 3 inches thick;

Fig. 30.

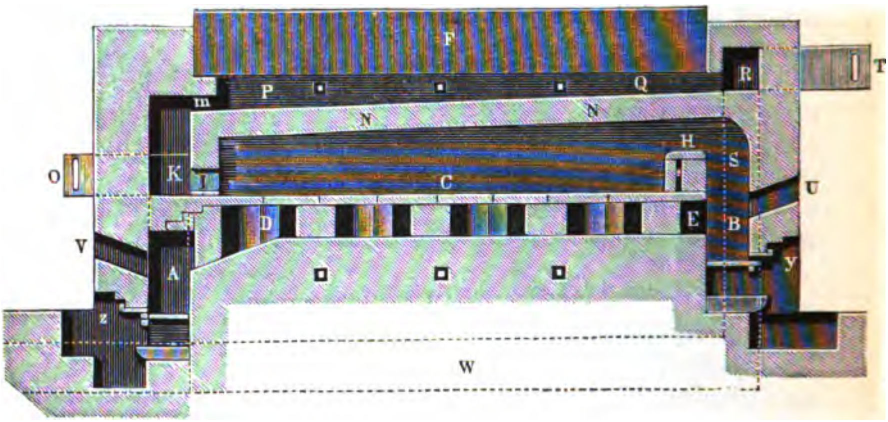



Fig. 31.

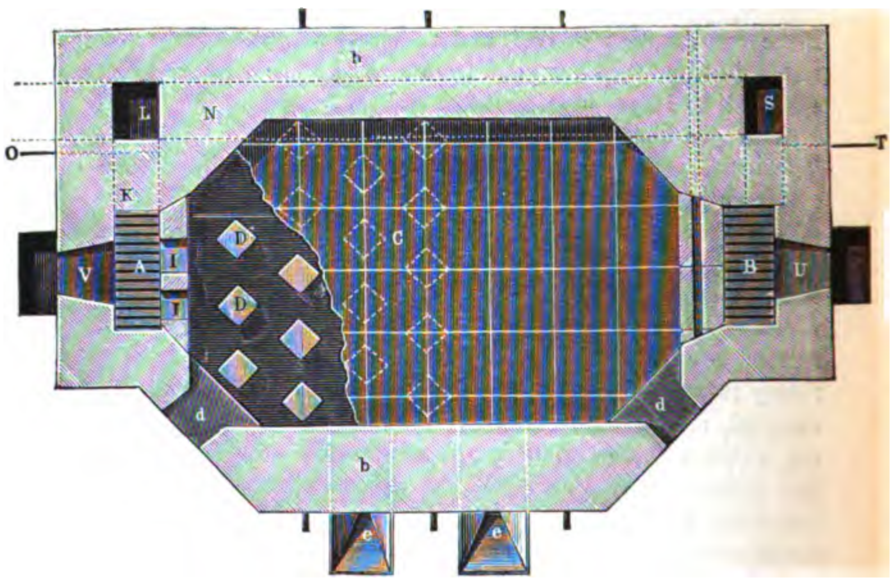
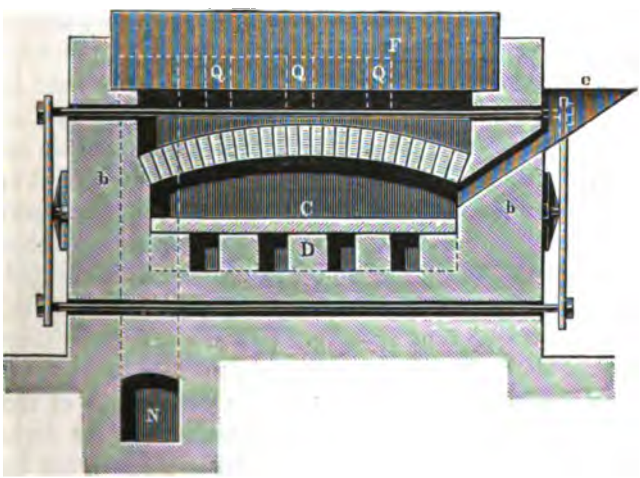


Fig. 32.


Fig. 33.




they rest upon 9 × 9 inch pillars 12 inches high, so placed that the flame of the fireplace A is uniformly divided below the bed. Round the sides the lumps rest on 2-inch projections of the walls. The lower flue DE, which is consequently as wide as the whole bed, and 12 inches high, at E joins into the second fireplace, B; here, below the fire-bridge H, the lower level rises up so that the flue is only 5 to 6 inches high. The united flame of both fires now travels over

the bed towards the snore-holes I I, and through these into the flue K. The latter communicates, 1st, with the flue L, which joins the main flue N, but it can be cut off by the damper O; 2nd, with the opening *m*, which admits the flame into the space P between the arch and the pans F. The draught is then continued by the snore-holes Q Q Q into the horizontal flue R, leading into the main flue past the damper S. When the damper T is shut, and O opened, the flame passes from the furnace directly into the main flue, without heating the pans; but when O is shut and T opened, the draught passes beneath the pans. The two fire-grates are of equal size, 3 feet long and 15 inches broad; the grates are composed of $1\frac{1}{4}$-inch wrought-iron bars; the stoke holes U and V are closed with fireclay slabs. The front wall of the fireplace W, 18 inches thick, is independent of the side walls and is carried on iron girders *y* and *z*, and closed by an arch X. By this arrangement it can be easily renewed without disturbing the other brickwork. The bridge H is cooled by an air-channel *s*, which has small openings at the side of the fireplace B. The side walls *b b* must have very secure foundations. The arch is 9 inches thick; the joints of the bricks run parallel with the long side of the furnace. The furnace is cased in metal plates $3 \times 2$ feet, bound together by uprights and tie-rods; that nearest the flame from *m* is protected by an iron or earthenware pipe. Cleaning-holes are provided for the flues K, R and the space below the bed between the pillars. The hopper *e* serves for charging the furnace. The furnace-bed has an area of about 100 square feet; it is 13 feet long and 8 feet wide. It is charged every two hours with 10 cwt. of mixture, daily with 6 tons of mixture, corresponding to $2\frac{1}{2}$ tons cryolite. [This is not the mixture with calcium fluoride.] The fuel consumed amounts to about 16 cwt. coals per diem, which also suffices for the evaporation of the soda-liquors to the crystallizing-point, and ultimately for drying the limestone on a metal plate. In this furnace the mass becomes red-hot all through, but no portion of it melts; so that it can be easily lixiviated. According to Thomsen, the decomposition of the cryolite is so nearly complete that from 100 parts of pure mineral 197 parts of crystal soda are obtained, the theoretical yield being 204 parts. [This statement, which is made for working without calcium fluoride, is directly contradicted by the above-quoted statements of Hagemann and Jörgensen; according to Bing (Wagner's Jahresb. 1862, p. 235), from 100 cryolite 175 soda

crystal are obtained, with a consumption of 37·5 coals.] If any lumps have been formed in spite of proper working in the furnace, they must be separated from the fine powder by riddling, and put back into the furnace with the next charge.

At Natrona 50 parts of finely ground and sifted cryolite are mixed with 10 parts of limestone and 40 of quicklime, and the mixture ignited in 16 Thomsen's furnaces, built back to back. Each charge amounts to 9½ cwt., and after igniting weighs 8¾ cwt.; six such are made per day [of 12 hours]. The mass is kept at a red heat for two hours, then drawn out and cooled on brick floors and sent to the lixiviating-apparatus.

The charge drawn out of the furnace is put while still hot into the lixiviating-tanks, made of wood, tapering below and provided with a perforated false bottom. The lixiviation is commenced with dilute liquors and mother liquors from former operations. The heat of the mass itself raises the temperature of the liquid; at last hot water is employed. The strong liquor shows 60° Tw.; the weaker liquor is employed for the next operation. At Natrona iron tanks (9 × 5 × 3½ feet) are used, and a liquor of 48° Tw. is obtained by using hot water containing sodium aluminate with a little carbonate and caustic; the lixiviation is finished with cold water, by which weak liquors are obtained. Sodium aluminate is dissolved out and pumped into the apparatus for treating it with carbonic acid; the residue, of a reddish colour, is principally calcium fluoride (formed in the operation), mixed with calcium carbonate, undecomposed cryolite, a little ferric oxide, and a little sodium aluminate. Its composition, according to Hagemann, is the following [but evidently the waste was examined after having been acted upon by the carbonic acid of the air]:—

| | per cent. |
|---|---|
| Calcium fluoride | 62·01 |
| „ carbonate | 11·89 |
| „ oxide | 5·62 |
| Potassium carbonate | 0·37 |
| Sodium „ | 3·94 |
| Magnesia | 0·93 |
| Silica | 3·78 |
| Ferric oxide | 5·00 |
| Alumina | 5·00 |
| Moisture | 1·45 |

At first this waste was only used for mending roads; but it is now considerably employed, partly for new mixtures (from which it is of course always recovered again), partly for bottle-glass: it makes the glass-mixture more easily fusible, permits a larger addition of lime, and thus yields stronger glass. Unfortunately the silicium fluoride acts too much upon the furnace-materials; so that no more than from 6 to 9 per cent. of the calcium-fluoride waste is put into the mixture. The glass retains 1·75 to 2·75 F; 1 per cent. of the fluorine volatilizes in the furnaces. The same waste furnishes a bluish-white enamel on stoneware and majolica. It is also used as a flux for metallurgical purposes, and as an admixture to fireclay for fire-bricks; these bricks are very hard, and resist the moisture very well.

The solution of *sodium aluminate,* which is brown, but free from iron and strongly alkaline, is sometimes boiled down to dryness and sold. There is, however, but very little sale for it; endeavours to introduce it into glass-making, calico-printing, &c., have failed. The liquor is therefore generally decomposed by forcing in carbonic acid, in closed boilers with agitators (at Natrona in revolving cylinders), and thus a precipitate of hydrated alumina (containing some soda) and a solution of sodium carbonate are obtained. The formula usually given is

$$Al_2O_3,\ 3Na_2O + 3CO_2 + 3H_2O = Al_2(OH)_6 + 3Na_2CO_3.$$

This, however, is not correct; for a real compound of 45 per cent. alumina, 20 per cent. sodium carbonate, and 35 per cent. water is precipitated in a finely granular readily settling state. The precipitate can be almost entirely deprived of soda by long washing with boiling water; but this makes the alumina gelatinous and difficult to treat. If alumina is to be sold as such, it must be washed down to 2 per cent. soda; otherwise, if sulphate is to be made from it, it is merely separated from the adhering liquor by centrifuging or by a vacuum filter and at once mixed with dilute sulphuric acid, in which it dissolves readily, especially when heated to 90° C. The solution of aluminium sulphate is boiled down in copper pans to the consistency of treacle, and poured into moulds, in which it solidifies into porcelain-like slabs, which are sold as *concentrated alum.* The alumina in it varies from 12 to 20 per cent.; the latter strength can only be obtained from cryolite. The usual formula $Al_2(SO_4)_3 + 18H_2O$ requires 15·31 per cent. $Al_2O_3$. According to

the mode of manufacture, both the alumina and the aluminium sulphate are almost entirely free from iron; and the latter is also easily obtainable free from an excess of acid. The strongest (20 per cent.) aluminium sulphate can be obtained in a porous form, greatly assisting its solubility, by stirring among the mass cast into the moulds, just before solidifying, a little sodium bicarbonate, from which $CO_2$ escapes at this temperature and causes the tough cake to be honeycombed by innumerable bubbles, like fermenting dough. This "Natrona porous alum cake" is much in favour with American consumers.

The sodium aluminate may also be converted by Loewig's process (Vol. II. p. 333) into caustic soda and "colloidal" alumina.

As a source of *carbonic acid* for decomposing the alumina the fire-gases from the cryolite-furnaces were formerly employed, containing also the $CO_2$ escaping from the limestone. But this gas is very impure, even mechanically; and by aspirating it the process in the furnaces is interfered with. It is therefore always made separately—at Oeresund by burning coke in a cryolite-furnace, at Natrona (formerly also at Golschmieden) by a lime-kiln fired with coke, of which figs. 34 to 37 give a representation.

Fig. 34.

Fig. 35.

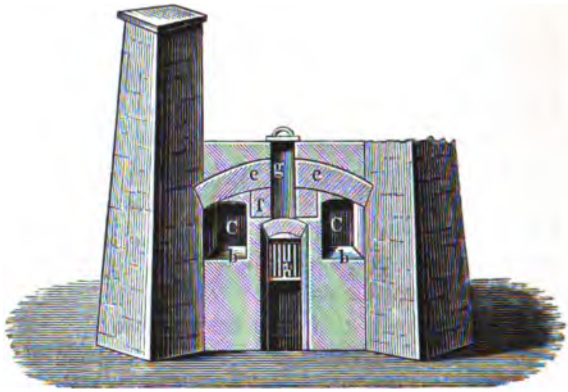



Fig. 36.

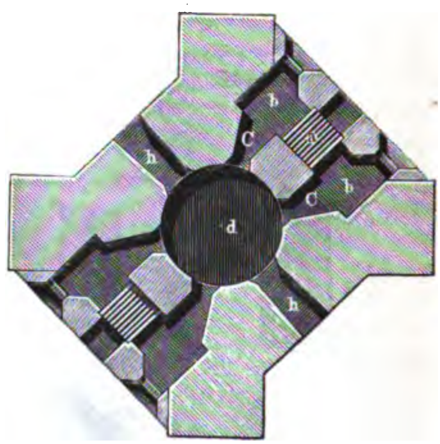
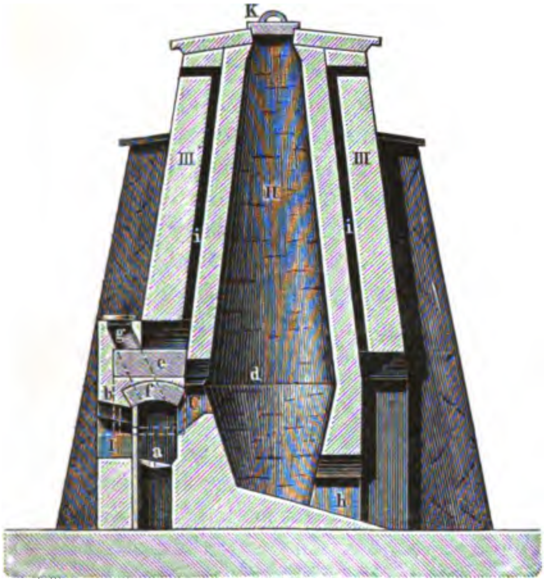


Fig. 37.




There are two opposite fireplaces, *a*, which in the place of a stoke-hole have an upright grate which can be taken out for cleaning the fireplace. The coke (gas-coke) is charged through *g* from above. The limestone is charged into the furnace-top through the opening usually closed by the cover *k*, and is burned to quicklime by the heat of the two fires *a*; the escaping $CO_2$, along with the fire-gases, is sucked off by the cast-iron pipe *l*, tapering from 7½ inches to 4¼ inches. At either side of each fireplace there are compartments, *b b*, communicating with the furnace-shaft by openings *e e*; through these the nearly burnt lime is drawn into the compartments *b b*, where it is allowed to be for six hours. The flame passes from *a* at both sides through the lime on the same way to the inner shaft. In these compartments the lime is finished burning, and then drawn out through doors at each side of the fireplaces, and an equal quantity of lime is then pulled from the shaft into the compartments *b b*; so that these always remain full. At *h* there are two opposite openings, tightly closed, through which some lime is discharged from time to time in order to remove the collecting dust. The limestone is charged in lumps of the size of

a fist, along with some pieces 1 or 2 feet in diameter. The gases from *l* first pass through a washing-apparatus under a pressure of 2 or 3 feet of water, and are aspirated from this by a double-acting air-pump with an 11-inch barrel and 16-inch stroke, and making 60 strokes per minute. The suction-pipe is 4¼ inches wide, the delivery-pipe 2¼ inches. The washing-apparatus is filled with pieces of limestone up to the water-level, which greatly diminishes the amount of water; the latter may be run in and out continuously. Here the impure $CO_2$ is purified, chiefly from tarry particles. A furnace of that kind supplies in 24 hours about 52 cubic feet of quicklime and sufficient $CO_2$ for saturating 10 cwt. of NaOH.

With a proper arrangement of the lixiviation the hot solution of *sodium carbonate* separated from the precipitated alumina is concentrated enough to crystallize on cooling; sometimes it must be first evaporated in pans on the top of the cryolite-furnaces. At Natrona it is boiled down to 66° Tw., and in winter run into the coolers to crystallize, but in summer into enormous reservoirs, holding up to 1000 tons of soda, made of cast-iron plates, where it remains through the winter. In spring the mother liquor is pumped out and the crystals broken out with ordinary mining-tools. The mother liquor can always be used again in the process, as it contains very little impurities. The crystal soda from cryolite is extremely pure; it contains at most ¼ per cent. of sodium sulphate, and formerly had to be assimilated to the common English soda by adding a little sulphate, as the consumers' prejudice required this. By treating it with quicklime, caustic of 75 per cent. $Na_2O$ can be made from it. Some calcined cryolite-soda analyzed by Tissandier (Monit. Scient. 1868, p. 909) contained:—

| | | | | |
|---|---|---|---|---|
| Moisture ........... | 2·06 | 3·28 | 4·61 | 0·89 |
| Sodium carbonate ... | 88·97 | 95·20 | 91·68 | 93·22 |

The Oeresund works consume annually 2000 tons, the Pennsylvania Salt-manufacturing Company 6000 tons of cryolite.

*Treatment of Cryolite with Lime in the wet way.*—This process, already indicated by Thomsen, was subsequently patented in England by Spilsbury (June 19th, 1856), who, however, never carried it out. In the same year Tissier (Wagner's Jahresb. 1857, p. 395) took it up; but he could only decompose one third of the cryolite in this way. Sauerwein proved (ib. 1862, p. 299) that complete decomposition can be attained by employing 6 molecules

of lime (=336 parts) to one molecule of cryolite (=447 parts). The same has been found by Hahn (Hofmann's 'Bericht,' 1875, i. p. 638), who gives some special prescriptions for the process, as well as Sauerwein. The latter worked in a complicated manner, which is of little interest now, as it has not stood the test of practical experience.

Wagner (his Jahresb. 1863, p. 343) proposed decomposing cryolite by baryta; but this is far too expensive to have any prospect of realization.

Schuch (Ann. Chem. Pharm. cxxvii. p. 61) proposed boiling cryolite with caustic-soda liquor, by which it is dissolved with formation of sodium aluminate and sodium fluoride. This never has been and is not likely to be carried out in practice.

Persoz (Ann. Chim. Phys. May 1859, p. 109) proposed the decomposition of cryolite by sulphuric acid, which was actually tried at Copenhagen, but given up again. To 1 molecule of cryolite, =476 parts, 6 molecules of sulphuric acid, =588 parts, are required, or 642 parts of ordinary strong vitriol, diluted with water. The products are aluminium sulphate, sodium sulphate, and hydrofluoric acid:

$$Al_2F_6,6NaF+6\,SO_4H_2=Al_2(SO_4)_3+3\,Na_2SO_4+12\,HF.$$

The great expense of vitriol, the evolution of HF, the difficulty of separating the sulphates of aluminium and sodium, and the small value of the latter make this process altogether worthless.

# CHAPTER XVIII.

## APPLICATIONS OF SODA*, AND STATISTICS.

The largest quantity of soda (alkali) is used for two manufactures which produce objects of daily use, viz. glass and soap. An enormous amount of crystal soda is used, partly under its own name, partly under sundry fancy names, for domestic washing; while soda ash is employed for the same purpose in factories, and for removing oil-paint. Very large quantities of alkali are also used in bleaching linen and cotton, scouring wool, dyeing, calico-printing, and paper-making; in the latter case it must be employed in the caustic state, except for rosin-soap. It further serves for preparing most sodium salts, especially the borate, phosphate, silicate, tartrate, sulphate (partly also hyposulphite), acetate, hypochloride, and in innumerable other cases in chemical manufacturing—also in the preparation of many kinds of colouring-matters, both mineral and organic (of the former, ultramarine is the chief). It further serves as a preventive of boiler-scales and in metallurgy (especially in steel-making). Altogether, it is employed wherever potash used formerly to be employed, except only in the case of those potash salts which have specific properties not found in the corresponding sodium salts—*e. g.* for Bohemian crystal, potash-alum, saltpetre, ferrocyanide of potash, chlorate of potash, soft soap. For English crystal (flint glass), potash was formerly considered indispensable; but here also it has been almost entirely replaced by the purer varieties of soda.

* The applications of caustic soda have been described in the 13th Chapter.

*Statistics of the Production of Soda.*

According to Williamson (Richardson and Watts's 'Chemical Technology,' iii. p. 318) the following figures respecting the British soda-manufacture in 1852 may be considered reliable:—

*Raw materials*:—

| | |
|---|---|
| Brimstone ........... | 11,520 tons. |
| Pyrites .............. | 100,262 „ |
| Salt .................... | 137,547 „ |
| Coals ................. | 519,420 „ |
| Nitrate of soda ...... | 4,800 „ |
| Manganese ......... .. | 12,000 „ |

*Manufactured articles*:—

| | | | |
|---|---|---|---|
| Soda ash.............. | 71,193 | tons, value | £711,930 |
| Soda crystals ......... | 61,044 | „ „ | 305,220 |
| Bicarbonate ......... | 5,762 | „ „ | 86,430 |
| Bleaching-powder ... | 13,100 | „ „ | 131,000 |
| | | | 1,234,580 |

Number of men employed, 6326.
Cost of plant, £702,000.
Annual cost of repairs, £129,700.
Tonnage of the sea-going vessels employed, 373,300.

In the year 1862 the following statements of Messrs. Henry Deacon, David Gamble, and John Hutchinson prove that the British alkali-manufacture had already doubled:—

Number of works, 50.

*Raw materials*:—

| | |
|---|---|
| Salt ............................ | 254,600 tons. |
| Coals .......................... | 961,000 „ |
| Limestone and chalk ......... | 280,500 „ |
| Pyrites ....................... | 264,000 „ |
| Nitrate of soda .............. | 8,300 „ |
| Manganese ..................... | 33,000 „ |
| Wood for casks .............. | 33,000 „ |
| | 1,834,400 |

*Manufactured articles* :—

| | |
|---|---|
| Soda ash ................. | 156,000 tons. |
| Soda crystals ............ | 104,000 „ |
| Bicarbonate ............ | 13,000 „ |
| Bleaching-powder ...... | 20,800 „ |

Value........... £2,500,000.

*Capital* employed :

| | |
|---|---|
| Value of ground........................... | £235,000 |
| „ plant ........................... | 950,000 |
| Working capital........................... | 825,000 |
| | 2,010,000 |

Annual value of material for repairs, £135,500.

| | | | |
|---|---|---|---|
| Number of men employed at the works | 10600, | wages | £549,500 |
| Number of men employed for getting raw materials ........................ | 8540, | „ | 322,250 |
| | 19140 | | £871,750 |

Worthless residues :

| | |
|---|---|
| Tank-waste, burnt ore, cinders, rubbish ... | 1,273,000 tons. |
| Hydrochloric acid running away, still-liquor, &c. ............................... | 2,600,000 „ |
| | 3,873,000 „ |

In 1867 there were made on the Tyne alone (according to Clapham, Acc. of Soda-Manufac. on the Tyne, p. 3) :—

*Raw materials* :

Pyrites, salt, chalk, wood, coals, manganese 1,070,000 tons.

Value........... £830,928.

(Of this, 157,000 tons of common salt.)

*Manufactured articles*:—

| | |
|---|---|
| Soda crystals .................. | 86,000 tons. |
| Soda ash ........................ | 74,000 „ |
| Bicarbonate ..................... | 11,000 „ |
| Sulphate of copper ............ | 200 „ |
| Sulphate of soda for sale...... | 2,400 „ |
| Bleaching-powder............... | 27,000 „ |
| Caustic soda........................ | 3,720 „ |
| Epsom salt ..................... | 590 „ |
| Crystallized Glauber's salt ... | 20 „ |
| Sulphuric acid for sale......... | 9,000 „ |
| Muriatic „ „ ......... | 700 „ |
| Hyposulphite of soda ......... | 400 „ |
| Chloride of manganese ...... | 1,300 „ |
| | 216,330 „ |

Value........... £1,929,825.

Number of men (on the Tyne), 8000.

Number of sea-going vessels employed, 5000.

Capital of works £2,000,000 to £2,500,000.

In Lancashire there were, in 1866, 26 alkali-works, which decomposed 194,000 tons of salt; the value of all the raw materials amounted to £869,600, that of the manufactured articles to £2,007,003, viz.:—

| | |
|---|---|
| Soda crystals .................. | 24,978 tons. |
| Soda ash ........................ | 87,314 „ |
| Caustic .......................... | 11,213 „ |
| Bicarbonate ..................... | 6,457 „ |
| Sulphate for sale ............... | 32,137 „ |
| Bleaching-powder............... | 20,006 „ |
| Bleach-liquor .................. | 5,871 „ |
| Sulphuric acid for sale......... | 18,592 „ |
| Muriatic „ „ ......... | 13,819 „ |
| | 220,387 „ |

Accordingly, both districts taken together, the values amounted to :—

| | |
|---|---|
| Raw materials ........... | £1,700,528 |
| Manufactured articles... | 3,936,828 |
| Capital employed........ | 5,000,000 |

The following Table, based on statements furnished by Messrs. Cail and Muspratt, is taken from Kingzett's 'History, Products, and Processes of the Alkali Trade,' 1877, p. 75 :—

| Salt decomposed. | | | | Exports of Alkali. | |
|---|---|---|---|---|---|
| Year. | Lancashire branch. | Tyne branch. | Total. | Quantity. | Value. |
| | tons. | tons. | tons. | cwt. | £ |
| 1860 ... | ...... | ...... | 250,000 | 2,049,582 | 965,348 |
| 1866 ... | 194,000 | 157,000 | 351,000 | 2,997,479 | 1,613,207 |
| 1869 ... | 164,922 | 141,983 | 306,905 | 3,514,382 | 1,379,108 |
| 1874 ... | 267,987 | 191,769 | 459,756 | 5,010,616 | 2,618,034 |

According to Clapham (Chem. News, xxxviii. p. 231), there were made on the Tyne, in 1877, 89,800 tons soda ash, 117,000 soda crystals, 7400 tons bicarbonate, 1500 tons caustic, 30,000 tons bleaching-powder.

For 1876, Mactear (Journ. Soc. Arts, 1878, p. 553) estimates the British alkali-manufactures as follows :—

*Raw materials* :—

| | | |
|---|---|---|
| Pyrites (incl. limestone) ... | 376,000 | tons. |
| Nitrate of soda.............. | 12,200 | „ |
| Common salt.................. | 538,600 | „ |
| Coals........................ | 1,890,000 | „ |
| Limestone and chalk ...... | 866,000 | „ |
| Manganese ................ | 18,200 | „ |
| | 3,701,000 | „ |

Number of men employed, 22,000.
Annual amount of wages, £1,405,000.
Capital employed, £7,000,000.

| | | |
|---|---|---|
| Soda manufactured (calculated as 48 per cent.) | 430,800 tons. | |
| „ exported (all strengths) .................... | 270,876 „ | |
| Value ........... | £2,209,284. | |

(In 1862 only 104,762 tons, of the value of £885,245, were exported.)

Great Britain exported alkali .—

| | In 1876. | In 1877. | In 1878. |
|---|---|---|---|
| Cwt......... | 5,546,191 | 5,656,597 | 5,647,035 |
| Value ...... | £2,222,866 | £2,181,741 | £1,973,473 |

Of this, to Germany :—

| | 1876. | 1877. |
|---|---|---|
| Cwt............... | 877,995 | 859,295 |
| Value ........... | £303,583 | £279,054 |

To America :—

| | 1876. | 1877. |
|---|---|---|
| Soda crystals ... | 16,500,000 lb. | 21,700,000 lb. |
| Soda ash ......... | 105,062,000 „ | 123,000,000 „ |

According to Jossinet (Chem. Industrie, 1878, p. 300), the annual consumption of salt (inclusive of that used in the ammoniacal soda-process) for alkali-works in France amounted, according to official statements, to

| | | |
|---|---|---|
| 116,687 | tons in | 1872 |
| 124,529 | „ | 1873 |
| 124,550 | „ | 1874 |
| 123,013 | „ | 1875 |
| 125,168 | „ | 1876 |
| 142,000 | „ | 1877 |

The French imports and exports amounted (in tons) to :—

| | Imports. | | | Exports. | | |
|---|---|---|---|---|---|---|
| | Soda crystals. | Soda ash. | Caustic. | Soda crystals. | Soda ash. | Caustic. |
| 1872 ......... | 4315 | 5670 | ...... | 360 | 5219 | ...... |
| 1873 ......... | 2433 | 5617 | ...... | 119 | 7054 | ...... |
| 1874 ......... | 4409 | 7906 | ...... | 796 | 6294 | ...... |
| 1875 ......... | 3253 | 5279 | 1553 | 652 | 7869 | 75 |
| 1876 ......... | 3607 | 5908 | 2364 | 844 | 6914 | 40 |

The German soda-manufacture is stated, in the Official Catalogue of the German Empire at the Vienna Exhibition, as follows :—

*Total make, in tons.*

| | Sulphate. | Soda ash. | Soda crystals. | Caustic. |
|---|---|---|---|---|
| 1867 ......... | 35767 | 26249 | 6027 | 890 |
| 1868 ......... | 34547 | 26106 | 5689 | 1054 |
| 1869 ......... | 36801 | 26644 | 6068 | 1332 |
| 1870 ......... | 36977 | 27407 | 6316 | 1473 |
| 1871 ......... | 41669 | 31168 | 6243 | 1685 |
| 1872 ......... | 51618 | 36227 | 6439 | 1986 |
| Number of works | 15 | 15 | 8 | 9 |

*Exportation into foreign countries, in tons.*

| | Sulphate. | Soda ash. | Soda crystals. | Caustic. |
|---|---|---|---|---|
| 1867 ......... | 733 | 112 | 92 | 63 |
| 1868 ......... | 766 | 116 | 92 | 134 |
| 1869 ......... | 966 | 119 | 100 | 222 |
| 1870 ......... | 933 | 119 | 116 | 302 |
| 1871 ......... | 1066 | 147 | 133 | 333 |
| 1872 ......... | 2600 | 187 | 166 | 322 |

According to Hasenclever (Chem. Industrie, 1878, p. 188), the importation into Germany, deducting the quantity exported, amounted (in tons) to :—

| | Soda ash. | Caustic. | Crystals. | Bicarbonate. | Total reduced to 52-per-cent. ash. |
|---|---|---|---|---|---|
| 1872 ...... | 7908 | 1165 | 11867 | 250 | 14382 |
| 1873 ...... | 10635 | 1915 | 13304 | 497 | 18908 |
| 1874 ...... | 16224 | 3867 | 11935 | 426 | 26495 |
| 1875 ...... | 16910 | 6165 | 12304 | 544 | 30481 |
| 1876 ...... | 15171 | 8073 | 14327 | 529 | 32092 |
| 1877 ...... | 15295 | ? | 11545 | ? | ? |

The total production of all the German alkali-works is estimated by Hasenclever at about 58,000 tons per annum (reduced to 53-per-cent. alkali), in 1877 at only 42,500. This does not quite agree with the official German returns, according to which there was, in 1876 :—

| | Imported. | Exported. |
|---|---|---|
| | tons. | tons. |
| Salt .................. | 123,000 | 165,500 |
| Bicarbonate ......... | 670 | 224 |
| Soda crystals ...... | 20,050 | 6,550 |
| Soda ash ............ | 23,750 | 11,300 |
| Caustic............... | 7,700 | 945 |
| Bleaching-powder . | 9,800 | 2,580 |
| Hydrochloric acid . | 1,595 | 5,800 |
| Brimstone ......... | 15,350 | 715 |
| Sulphuric acid...... | 7,200 | 9,100 |
| Sulphate of soda ... | 1,325 | 2,665 |
| Nitric acid ......... | 238 | 640 |
| Nitrate of Soda ... | 48,050 | 5,900 |

Official reports state the quantity of salt consumed in the fiscal year 1877–78 in Germany at 80,667 tons.

The last two years' returns for Germany are :—

| | Imported. | | Exported. | |
|---|---|---|---|---|
| | 1877. | 1878. | 1877. | 1878. |
| | tons. | tons. | tons. | tons. |
| Soda ash ........... | 16,625 | 16,054 | 1,653 | 1,702 |
| Soda crystals ...... | 15,752 | 15,013 | 4,257 | 5,047 |

According to 'Chem. Industrie,' 1879, p. 267, there existed then in Germany twenty-one alkali-works, with a capital of £2,200,000, employing 6619 workmen and 361 officials; they worked up 600,000 or 650,000 tons of raw materials, costing £575,000, and paid for freights £185,000, for wages £300,000.

It should be mentioned that the quantity of *caustic* soda made in Germany is rapidly increasing, and at the same time the quality both of this article and of calcined soda ash has made rapid strides in improvement; so that even the returns of the last year, if ready, would present a different picture from the above.

The *United States* imported, in pounds :—

| | In 1872. | In 1873. | In 1874. | In 1875. | In 1876. | In 1877. |
|---|---|---|---|---|---|---|
| Sulphate of soda ................. | 7,070 | 62,182 | 169,046 | 71,593 | 11,718 | 285 |
| Soda ash ........................ | 143,177,508 | 188,443,202 | 149,203,789 | 170,892,671 | 165,502,897 | 200,631,499 |
| Soda crystals .................... | 21,587,244 | 27,237,478 | 31,126,647 | 27,666,534 | 20,074,269 | 18,648,665 |
| Bicarbonate ...................... | 13,530,188 | 10,571,049 | 11,873,182 | 6,853,588 | 4,482,911 | 3,765,165 |
| Caustic soda ..................... | 29,992,539 | 28,871,629 | 34,282,189 | 37,669,885 | 32,093,691 | 33,375,447 |
| Bleaching-powder ............... | 35,043,050 | 44,155,383 | 39,184,641 | 48,433,540 | 46,934,185 | 47,592,989 |
| Chlorate of potash ............. | 609,821 | 696,261 | 804,346 | 755,791 | 474,598 | 1,122,442 |

# FOURTH BOOK

## BLEACHING-POWDER

AND

## CHLORATE OF POTASH.

# CHAPTER I.

## GENERAL.

The bleaching- and the soda-industry, as we have already seen, are intimately connected; for by far the largest portion of the hydrochloric acid arising as a by-product in alkali-making is worked up for bleaching-compounds. The present low price of soda ash is only possible by the profit made in manufacturing bleaching-powder. It is a remarkable coincidence that the discovery of chlorine and of chloride of lime happened about the same time as the invention of artificial soda and the working-out of Leblanc's process, so that from the first both industries could proceed hand in hand. The gas given off by aqua regia, which contains chlorine, was already known to Van Helmont; Glauber also (1648) and Boyle (1661) seem to have had it under their hands; but the undisputed discoverer, properly so called, of chlorine itself was Scheele, who described it in his treatise on manganese, in 1774, mentioning at the same time its bleaching action on vegetable colours. He did not take it for an element, but for "dephlogisticated muriatic acid." The hydrate of chlorine was discovered in 1785 by Pelletier, and in 1786 by Karsten, both of whom took it for solid chlorine, till Davy showed, in 1810, that it contains water. Faraday, in 1823, analyzed it quantitatively, and on that occasion obtained chlorine condensed to a liquid.

The industrial employment of the bleaching-properties of chlorine, discovered by Scheele, was first suggested by Berthollet in 1785. He at first used chlorine-water; but from 1789 the chlorine was passed into potash-liquor at the Javelle works near Paris, whence chloride of potash is still called "eau de Javelle." Here

the celebrated James Watt saw the new bleaching-process, and in 1786 introduced it into the works of his relative MacGregor at Glasgow. It would appear that already in July 1787 Milnes and Gordon, Barrow, and Co., at Aberdeen had employed chlorine for bleaching on a large scale, in consequence of the observations made by Professor Copeland and the Duke of Gordon in France (Mactear, Report &c., p. 16; Kingzett, 'Alkali Trade,' p. 180). According to Keyworth (Chem. News, xxxiii. p. 131), Robert Hall, of Basford Hall, near Nottingham, had been the first to apply chlorine on a manufacturing-scale to the bleaching of fabrics; but as no date is given, this statement is of little account. On March 25th, 1789, de Boneuil patented for England the manufacture of chlorine-water and its application for bleaching; the same was again done by C. and G. Taylor on April 25, 1792, by Campbell on Nov. 28, 1792, by Bigg on Feb. 28, 1795 (application to paper-stuff), by Lord Dundonald on the same day; and by Carpenter on Nov. 19, 1795. But the most important step was taken by Charles Tennant, in his patent of Jan. 23rd, 1798. In this he describes the employment of lime, strontia, or baryta, instead of alkalies, for "neutralizing the oxy-muriatic acid," but only suspended in water; so that he obtained the compound at present known as "bleach-liquor." Tennant at that time carried on a bleach-works at Darnley; and he soon commenced manufacturing bleach-liquor in partnership with MacIntosh. This was already a vast improvement, since the then enormously dear alkalies were replaced by milk of lime; but the still greater advance, the employment of dry calcium hydrate instead of milk of lime, and consequently the preparation of a more stable and more portable form of bleaching-compound, was made in the following year, after Tennant's patent had been invalidated owing to some error in form. He now took out a fresh patent (on April 30, 1799), for absorbing chlorine by dry hydrate of lime (baryta, or strontia), and in the same year started the St.-Rollox works near Glasgow, which are probably to this day the largest bleaching-powder works. From the tables given by Mactear (*op. cit.* p. 18) it appears that 52 tons, at a price of £140 per ton, were manufactured in 1799–1800; in 1805 only 147 tons at £112; in 1820, 333 tons at £60; in 1825 (muriatic acid being already employed), 910 tons at £27; in 1870, 9251 tons at £8 10*s*.

## *Chlorine.*

We have already seen that chlorine was discovered by Scheele in 1774. He called it dephlogisticated muriatic acid, to which name Berthollet's designation of oxymuriatic acid corresponds. The radical of muriatic acid was itself believed to be a compound body, being supposed to contain oxygen. Many chemists adopted this view; but it was shaken when Gay-Lussac and Thénard in 1806 could not isolate any oxygen from chlorine. Still Berthollet's view of the compound nature of chlorine was adhered to, till Davy in 1810 adduced new arguments for its elementary nature, and gave it the name "chlorine" (from χλωρός, green). Davy himself pointed out that his view was not essentially different from that of Scheele. Most chemists adopted Davy's explanation at once; but some opposed it, especially Murray (1811) and Berzelius (1812–15); and it was only in 1821 that the latter, and the rest with him, finally came over to Davy's view, which, however, has been shaken to a certain extent by the researches of V. Meyer (see below).

The colour-destroying compounds which chlorine forms with aqueous solutions of the alkalies were first recognized by Berthollet; they were especially examined by Balard (1831), who also discovered free hypochlorous acid. Berthollet also prepared some chlorates; Gay-Lussac, in 1814, free chloric acid.

Chlorine occurs very extensively in all three natural kingdoms; we are here only interested in its occurrence as sodium or potassium chloride and hydrochloric acid, because these only are employed as technical sources for preparing chlorine. It is always either made from hydrochloric acid by treating it with manganese peroxide (rarely by potassium bichromate), or from sodium chloride and sulphuric acid. The latter was the general means of preparing it so long as muriatic acid had a higher price. Not only manganese peroxide, but also a number of other bodies, easily parting with their oxygen, evolve chlorine with hydrochloric acid—such as the potassium bichromate already mentioned, lead peroxide, nitric acid, &c.; for technical purposes, or even for laboratory use, the latter cannot be employed. The various plans which have been proposed are treated in the 4th Chapter.

Chlorine is a greenish-yellow gas, and is darker in proportion as it is hotter. Its specific gravity, calculated from Stas's atomic weight, is 2·45012; it was observed by Bunsen to be = 2·4482.

This, however, only refers to temperatures up to about 600°. In July 1879 Professor Victor Meyer, of Zurich (Ber. d. deutsch. chem. Ges. xii. p. 1426), assisted by C. Meyer, found that from 800° upwards the specific gravity of chlorine (prepared by heating platinous chloride) diminishes until at 1200° it becomes constant again; and then up to the highest temperature observed, viz. 1567°, it varies only between the limits of 1·60 and 1·66. This fact proves with certainty that dissociation has taken place, 1·63 being precisely two thirds of the theoretical specific gravity of chlorine at lower temperatures, as stated above. This evident dissociation can be explained in one of two ways. It may be assumed that, what has been hitherto considered an atom of chlorine is in truth a group consisting of three atoms of a new trivalent element, chlorogen, of the atomic weight $\frac{35 \cdot 5}{3} = 11 \cdot 8$, say $\begin{matrix}\mathrm{Cg}\\ \| \\ \mathrm{Cg}\end{matrix}\!\!>\!\mathrm{Cg}—$, the molecule being $\begin{matrix}\mathrm{Cg}\\ \| \\ \mathrm{Cg}\end{matrix}\!\!>\!\mathrm{Cg}—\mathrm{Cg}\!<\!\!\begin{matrix}\mathrm{Cg}\\ \| \\ \mathrm{Cg}\end{matrix}$. This would explain the monatomic nature of chlorine—two such groups combining to form a molecule of chlorine at the ordinary temperature, which above 600° dissociates into three groups or molecules:

$$2\begin{matrix}\mathrm{Cg}\\ \| \\ \mathrm{Cg}\end{matrix}\!\!>\!\mathrm{Cg}—\mathrm{Cg}\!<\!\!\begin{matrix}\mathrm{Cg}\\ \| \\ \mathrm{Cg}\end{matrix} = 3\begin{matrix}\mathrm{Cg}—\mathrm{Cg}\\ \| \quad\quad \| \\ \mathrm{Cg}—\mathrm{Cg}\end{matrix}.$$

It also explains the tri-, quinqui-, and septivalent nature of chlorine under certain circumstances by a solution of the internal bonds, and a large number of facts generally. On the other hand, it is quite as probable that the old murium theory, for which a large array of reasons can be quoted, and which has been persistently adhered to by some distinguished chemists (*e. g.* Schönbein), is true after all; so that chlorine would be the peroxide of a hypothetical element, murium, the monoxide of which would be the hypothetical muriatic anhydride, which with water yields hydrochloric acid, thus:—

| | |
|---|---|
| Chlorine (murium peroxide) ... | $\left.\right\} \begin{matrix}\mathrm{Mu}—\mathrm{O}\\ \quad\ \ | \\ \mathrm{Mu}—\mathrm{O}\end{matrix}$ |
| Muriatic anhydride ........... | $\begin{matrix}\mathrm{Mu}\\ \mathrm{Mu}\end{matrix}\!\!>\!\mathrm{O}$ |
| Hydrochloric acid .............. | MuOH |

The experiments instituted by V. and C. Mayer, in order to settle the point whether oxygen is actually liberated or not in the above case, could not decide the question with certainty, owing to the very great experimental difficulties encountered. Other chemists have explained the results of Meyer in a different way, viz. by an alteration of the rate of expansion of chlorine at higher temperatures (Lieben, Compte Rendus, Aug. 11, 1879), or, much more likely, by a partial dissociation of the molecule of chlorine into atoms (Crafts, ib. vol. xl. p. 183). Meyer himself found afterwards (Ber. deutsch. chem. Ges. xiii. 399) that the vapour-density of chlorine, employed as a free gas, not in the nascent state as it is evolved from platinous chloride, is quite normal, viz. 2·45; and *Craffts* (l. c.) had found and published the same fact independently. Both chemists, however, found that iodine (whose close analogy to chlorine nobody can doubt) shows a diminution of vapour-density even when employed in the free state; according to Craffts it seems to possess only 60 per cent. of its normal vapour-density at a temperature of about 1400° C.; so that here, at any rate, a splitting up of the molecule must needs be assumed.

In the anhydrous state chlorine has not yet been solidified under ordinary pressure at −40° C.; but under a pressure of 4 atmospheres already at +15° C. it forms a clear yellow liquid of spec. grav. 1·33, which does not freeze at −90° C., and boils at −33°·6 under a pressure of 760 millims. Chlorine gas is not combustible, but supports the combustion of many organic compounds with a strongly fuliginous flame. It does not act upon dry litmus-paper when perfectly dry itself, but in the moist state destroys its colour, as well as most other vegetable dyes. It also destroys organic smells and infectious matters, and is consequently of great importance as a disinfectant. Its smell is extremely suffocating; it causes, when respired in very slight quantity, cold in the head, general irritation of the epithelium, coughs, suffocating attacks, vomiting, and, if more frequently breathed, spitting of blood. As an antidote, the breathing of sulphuretted hydrogen, alcohol or ether vapour, or aniline vapour is recommended; the workmen employ rum as an internal remedy.

Chlorine occurs uni-, tri-, quinqui-, and septivalent, viz. univalent in all chlorides and organic compounds, tri- to septivalent in its oxides. Its atomic weight has been frequently determined—most

accurately by Stas, whose result (oxygen=16) is 35·457 or (hydrogen=1, oxygen=15·96) =35·368. For calculations 35·5 is usually assumed. A litre of it at 0°C. and 760 millims. weighs 3·170 grams. Its chemical affinities in most cases are much more energetic than those of oxygen. Equal volumes of chlorine and hydrogen mixed together are caused to combine not only by the electric spark or a red-hot body, but even by the sunlight, with a violent explosion.

At a little above 0° C. chlorine combines with water and forms a solid mass. From saturated chlorine-water in the cold there crystallizes *chlorine hydrate*, $Cl+5H_2O$, or $Cl_2+10H_2O$, with 28·29 per cent. chlorine. Göpner (Deutsch. chem. Ges. Ber. viii. p. 287) assigns to it the formula $HOCl,HCl,9H_2O$, *i. e.* a common hydrate of hydrochlorous acid and hydrochloric acid. Schiff (*ib.* p. 419), to whom Göpner referred, declines this view, since such a concentrated solution of hypochlorous acid is quickly decomposed at 20° C., and it is not conceivable that the presence of a molecule of HCl should convert it at 10° C. into such a stable compound as chlorine hydrate. This forms an arborescent, crystalline, pale yellow, transparent mass of specific gravity about 1·2; Faraday observed it in needles and rhombic octahedra, Biewend in tesseral crystals. At −50° C. it is almost white. At the ordinary temperature and pressure it dissociates into chlorine gas and chlorine-water; in sealed tubes it remains unchanged even in the heat of summer; but at +38° it splits up into chlorine-water and liquid chlorine. (The dissociation of chlorine hydrate has been fully investigated by Isambert, Compt. Rend. lxxxvi. p. 481.) This hydrate is frequently formed in winter in the pipes conveying the gas in bleaching-powder-works when exposed to the cold, and sometimes stops up the pipes completely.

Water absorbs chlorine gas most amply at 10° C.; from 9° to 0° its solubility decreases, because it is then in the state of hydrate. At 0° C. one part of water dissolves 1·43 (Gay-Lussac) or 1·80 (Pelouze) part of chlorine. At 100° its solubility is =0. Saturated chlorine-water at 6° has the specific gravity 1·003; it is greenish yellow, smells of chlorine, and has an astringent but not acid taste. It freezes at 0°, and splits up into chlorine hydrate and ice free from chlorine.

According to Schönfeld (Ann. Chem. Pharm. xciii. p. 26, cxv. p. 8),

the coefficient of absorption of chlorine gas from 11° to 41°·5 C. is $= 3{\cdot}0361 - 0{\cdot}046196\,t + 0{\cdot}0001107\,t^2$. According to him 1 vol. of water absorbs the following volumes of chlorine (calculated at 0°C. and 760 millims.):—

| At | Vols. of chlorine. | At | Vols. of chlorine. | At | Vols. of chlorine. |
|---|---|---|---|---|---|
| 10°C... | 2·5852 | 21°C... | 2·1148 | 31°C... | 1·7104 |
| 11...... | 2·5431 | 22...... | 2·0734 | 32...... | 1·6712 |
| 12...... | 2·4977 | 23...... | 2·0322 | 33...... | 1·6322 |
| 13...... | 2·4543 | 24...... | 1·9912 | 34...... | 1·5934 |
| 14...... | 2·4111 | 25...... | 1·9504 | 35...... | 1·5550 |
| 15...... | 2·3681 | 26...... | 1·9099 | 36...... | 1·5166 |
| 16...... | 2·3253 | 27...... | 1·8695 | 37...... | 1·4785 |
| 17...... | 2·2828 | 28...... | 1·8295 | 38...... | 1·4406 |
| 18...... | 2·2405 | 29...... | 1·7895 | 39...... | 1·4029 |
| 19...... | 2·1984 | 30...... | 1·7499 | 40...... | 1·3655 |
| 20...... | 2·1565 | | | | |

Chlorine, mixed with H or $Co_2$ is absorbed by water more largely between 13° and 38° than corresponds to its partial pressure (Roscoe). Chlorine-water decomposes gradually, especially in the light, into hydrochloric acid and oxygen gas.

The affinity of chlorides for oxygen is very slight; they cannot be directly combined. Indirectly, however, a number of compounds of chlorine with oxygen only (anhydrides) and with both oxygen and hydrogen (the acids of chlorine) are obtainable. Of these we are at present only interested in *hypochlorous acid*, ClOH, and its anhydride ClOCl. Chlorine yields hypochlorites with aqueous solutions of the alkalies and alkaline earths, or with their hydrates containing a little water. When chlorine is not in excess, chloride and hypochlorite are formed from the alkaline hydrates; with an excess of chlorine, chloride, and free hydrochlorous acid:— the former according to the equation

$$2KOH + 2Cl = KOCl + KCl + H_2O;$$

the latter according to

$$KOH + 2Cl = KCl + HOCl.$$

According to Blomstrand (Gmelin-Kraut, i. 2, p. 353), at first

hypochlorite and hydrochloric acid are formed

$$(KOH + 2Cl = KOCl + HCl);$$

the HCl then saturates a second molecule of potash. According to Williamson (*ib.*), caustic potash-liquor, on being supersaturated with chlorine and shaken in the air, absorbs $1\frac{1}{2}$ eq. chlorine; the bleaching-liquid contains *no* salt of hypochlorous acid, but already chloric acid or potassium chlorate. Baryta-water, saturated with chlorine and shaken with air, absorbs 4 eq. chlorine, and then contains barium chloride and free hypochlorous acid

$$Ba(OH)_2 + 4Cl = BaCl_2 + 2HOCl,$$

but no barium hypochlorite, since $CO_2$ does not cause a precipitate, and silver nitrate yields a white precipitate, not, as with hypochlorites, a black one. Hence the hypochlorite at first produced must be completely decomposed by further chlorine:

$$Ba(OCl)_2 + 4Cl + 2H_2O = BaCl_2 + 4HOCl.$$

According to Konigel-Weisberg (Ber. d. deutsch. chem. Ges. xii. pp. 346, 511), dry barium hydrate is not affected by chlorine. In the presence of water, one molecule of BaO will absorb two molecules of Cl. Any hypochlorite at first formed decomposes quickly into chlorate and chloride, which two form the final products. Strontia behaves exactly in the same way. The action of chlorine on calcium hydrate is more complicated, and will be explained afterwards in connexion with bleaching-powder.

If chlorine is passed through water in which finely powdered chalk is suspended, this is dissolved as $CaCl_2$, $CO_2$ escaping, and aqueous HOCl being formed, which can be distilled off (Williamson; Kolb: the equation should be

$$CaCO_3 + H_2O + 4\,Cl = CaCl_2 + CO_2 + 2\,HOCl;$$

but under such circumstances hypochlorous acid is quickly transformed into chloric acid). Chlorine, passed into the solution of an alkaline carbonate, produces chloride along with free HOCl according to some, or hypochlorite according to others. Hypochlorous acid can in no case expel $CO_2$ from carbonates, except by its own decomposition, and hence does not cause any effervescence in a solution of sodium carbonate [this is contradicted by Walters, Wagner's Jahresb. 1874, p. 347], or any precipitation of bicar-

bonate; in the presence of alkaline carbonates it retains its smell and its bleaching-property. If only just too little chlorine is passed through a solution of $Na_2CO_3$ to produce any effervescence, a pale yellow liquid is obtained, smelling faintly of chlorine, by which turmeric-paper is first reddened and then bleached; it loses scarcely any of its bleaching-power on boiling, but much on evaporation to dryness; and the quicker the evaporation the greater the loss. If a solution of $Na_2CO_3$ be supersaturated with chlorine, a yellow, strongly bleaching liquor is obtained, which, when evaporated in a thin layer in warm air, leaves a residue by which turmeric is first turned brown and then decolorized, which therefore, in spite of the excess of chlorine, still contains sodium carbonate. On boiling, this liquid evolves chlorine, loses its colour, and leaves on evaporation sodium chloride, chlorate, and a little carbonate (Gmelin-Kraut, *l. c.*). The anhydride $Cl_2O$ is a blood-red liquid, of violent chlorine-like smell, boils at 19–20° C., and is easily decomposed even at ordinary temperatures, often with an explosion. Water at 0° C. absorbs more than 200 vols. of the gas, the hydrate $ClOH$ being formed. The aqueous acid can be made, as mentioned, by passing chlorine gas into chalk suspended in water and distilling, or by shaking chlorine gas with mercuric oxide suspended in water, or by incompletely saturating bleaching-powder with very dilute nitric acid, and distilling. The concentrated aqueous acid has the smell of the gas and a strong taste, and a highly caustic action on the skin. In the air it volatilizes almost entirely. The concentrated acid, on being heated, gives off a reddish-yellow gas; the diluted acid at 100° C. only a little gas, but much more on adding calcium nitrate or phosphoric acid: concentrated sulphuric acid decomposes it into chlorine, hypochloric acid, and a little oxygen. The dilute acid decomposes slowly even in the dark, and the more quickly the more concentrated and hot it is; concentrated acid will keep only for a few days, even if surrounded by ice; it yields chlorine and chloric acid. In light the decomposition proceeds more rapidly. The dilute acid can be concentrated by fractional distillation, the stronger acid passing over first; but here also chlorine, oxygen, and chloric acid are formed, especially from the concentrated acid.

The solution of hypochlorous acid is a very powerful oxidizing agent, dissolving many metals up to the maximum of their oxygenation or chlorination; it also decomposes many organic compounds.

The *Hypochlorites* of the alkaline metals, of magnesium, zinc, and copper, can be obtained by mixing the hydroxides with dilute ClOH The solutions, when containing carbonate in excess, can be dried down at the ordinary temperature *in vacuo* without decomposition. Much more frequently hypochlorites are obtained mixed with chlorides by admitting no more than an equivalent of chlorine to the aqueous solution or suspension of the alkalies, alkaline earths, or magnesia at a low temperature. Too high a temperature or an excess of chlorine causes decomposition (see above). Formerly the solutions thus obtained were believed to contain direct compounds of chlorine with the alkalies &c.—*e. g.* $Na_2OCl_2$, $CaOCl_2$. Berzelius already in 1808 pronounced them to be mixtures of a chloride and a salt of an acid of chlorine; and since Balard's discovery of hypochlorous acid they are generally regarded as mixtures of chlorides and hypochlorites—*e. g.*

$$NaCl + NaOCl, \text{ and } CaCl_2 + Ca(OCl)_2.$$

With *solid* chloride of lime the case is different, as we shall see.

The hypochlorites, MOCl, have a caustic and astringent taste; they do not produce any white spots on the skin, and in contact with organic substances have a peculiar faint smell. That their smell is not attributable to free hypochlorous acid, as usually assumed, we shall see later on. In the dark at the ordinary temperature they give off oxygen very slowly; in daylight (and much more quickly in sunlight) the solutions of the alkaline hypochlorites decompose into chloride, chlorite, and chlorate, with evolution of oxygen. A solution of chloride of lime, when kept in a closed vessel, gradually gives off oxygen, especially in daylight, and leaves $CaCl_2$ behind; in direct sunlight chlorite also is formed, along with a little chlorate. On heating the aqueous solution, even *in vacuo*, if the alkali does not greatly predominate, the alkaline hypochlorites are decomposed, mostly with evolution of oxygen, into chloride and chlorate. But with an excess of alkali, alkaline hypochlorites can be evaporated even at 50° C. without decomposing into chloride and chlorate; the residue still bleaches strongly. Solutions of chloride of lime are by long-continued boiling converted into calcium chloride and chlorate: during this no oxygen escapes if the solution contained only 16 grams $CaO_2Cl_2$ per litre; but from solutions containing 22, 32, and 48 grams $CaO_2Cl_2$ per litre only 80·5, 48·4, and 43·8 per cent. $Ca(ClO_3)_2$ are obtained,

because oxygen is lost (Schlieper, Ann. Chem. Pharm. c. p. 171). Gay-Lussac and Mitscherlich already noticed that the evolution of oxygen on boiling solutions of bleaching-powder was increased by the addition of powdered manganese, ferric oxide, cupric oxide, &c., without these substances themselves being decomposed. Fleitmann (Ann. Chem. Pharm. cxxxiv. p. 64) observed that concentrated solutions of bleaching-powder are completely decomposed into calcium chloride and oxygen on being heated with a trace of cobalt peroxide; and this reaction has often been employed for making oxygen. Several other substances act in the same way (Gmelin-Kraut, i. 2, p. 359).

The action of an excess of chlorine on hypochlorites at the ordinary temperature is of practical importance. By this free hypochlorous acid is obtained, *e.g.*

$$KOCl + 2\,Cl + H_2O = KCl + 2\,HOCl.$$

Bleaching-powder also behaves in this way; and the presence of free hypochlorous acid can be proved by distillation. Herein, even at the ordinary temperature, according to Balard chlorate is formed, but according to Martens and Kolb very little or none. It is established, however, that the conversion of hypochlorites into chlorate by heating is very much hastened by the presence of an excess of chlorine; and since, under such circumstances, where by an excess of chlorine free hypochlorous acid is formed a rise of temperature can hardly be avoided, there is nearly always a noticeable, and sometimes a predominant formation of chloric acid.

The hypochlorites act as oxidizers in the same way as the free acid, and raise most of the lower oxides to the highest degree of oxidation. They destroy organic colouring-matters and smells (*i. e.* they bleach and disinfect), though only slowly and to a small extent when other acids are entirely excluded. The hypochlorites, however, may exert an oxidizing and consequently a bleaching action even without HOCl or Cl becoming free: *e. g.*

$$CaS + 2\,Ca(OCl)_2 = CaSO_4 + 2\,CaCl_2.$$

It is indeed possible to bleach fabrics or paper-pulp completely in closed vessels in the absence of air; but certainly the oxidizing and bleaching action of hypochlorites takes place much more readily with the assistance of acids, even of the weakest: carbonic acid, for instance, causes a strong action of this kind, as, like the

other acids, it sets hypochlorous acid free. When $CO_2$ acts upon dissolved or moistened bleaching-powder, the HOCl becomes free and all the lime combined with it is precipitated as carbonate. An insufficient quantity of sulphuric or nitric acid also causes the liberation of hypochlorous acid from hypochlorites; but hydrochloric acid, or an acid decomposing chlorides with separation of HCl, yields both chlorine and free hypochlorous acid; and of course the same thing happens when from the first a sufficient excess of strong acid is added:

$$KOCl + NO_3H = KNO_3 + HOCl;$$
$$KOCl + KCl + SO_4H_2 = K_2SO_4 + H_2O + 2\,Cl;$$
$$KOCl + 2\,HCl = KCl + H_2O + 2\,Cl.$$

[The above statements on the reactions of hypochlorous acid and its salts, chiefly taken from Gmelin-Kraut, must be supplemented by the researches of the last few years, mentioned below.]

The action of ammonium chloride upon bleaching-powder has been studied by Salzer (Dingl. Journ. ccxxx. p. 418). The two substances, shaken together in the dry state, give off an explosive gas, probably by the decomposition of ammonium hypochlorite. Pure and saturated bleaching-powder (38 per cent. chlorine) does not yield any free ammonia with ammonium chloride if dry, but only after it has become moist; this seems to prove that no free lime is present. After triturating such bleaching-powder with 100 times its weight of water and adding a neutral solution of ammonium chloride in excess, a perfectly clear, neutral, not bleaching liquid is formed, which gradually gives off gas and turns acid.

The only hypochlorite obtained in a *crystallized* state is that of calcium, described by Kingzett (Chem. News, xxxi. p. 113; xxxii. p. 21). He caused a filtered solution of bleaching-powder to freeze in a refrigerating-mixture, and allowed the solid mass obtained to thaw on a filter, by which he obtained feathery crystals almost an inch long; he also obtained the crystals by allowing the solution to stand in a vacuum beside sulphuric acid or caustic potash. They are very unstable, and in the air lose chlorine or hypochlorous acid. According to Kingzett's analyses they are $Ca(OCl)_2 + 4H_2O$; but those analyses are not sufficiently concordant to make certain the exactness of that formula. This "crystallized calcium hypochlorite" must therefore be examined further before its existence can be pronounced indubitable. Kingzett points out that this

product has the great advantage over bleaching-powder of being entirely soluble in water and containing the bleaching chlorine in a much smaller volume. But these advantages are of very little moment, looking at the extremely slight stability of the salt; and, moreover, its discoverer himself says he is unable to indicate a technically available process for its production.

### *Chloride of Lime (Bleaching-Powder).*

We have already mentioned this product several times, but have almost exclusively described the reactions of its solution, in which, almost universally, calcium hypochlorite is assumed to be present along with calcium chloride; and the product obtained by absorption of chlorine in milk of lime (bleach-liquor) behaves in just the same way; but the product obtained by absorption of chlorine by slaked lime, the bleaching-powder itself, must be submitted to a special consideration, since opinions widely differ as to its constitution.

At first and for some time after the discovery of bleaching-powder it was assumed to be simply a compound of chlorine and lime, according to modern atomic weights = $CaOCl_2$. Balard in 1835 (Ann. Chem. Phys. [2] lvii. p. 225), after discovering hypochlorous acid and studying the alkaline hypochlorites, came to the conviction that bleaching-powder is a compound or mixture of equivalent proportions of calcium hypochlorite and chloride, $= CaO_2Cl_2 + CaCl_2$, mixed with an excess of calcium hydrate. In a research of Gay-Lussac's in 1842 (ib. [3] v. p. 273) Balard's formula was confirmed by new arguments; and down to the last few years it was almost universally assumed that not merely the solution, but also solid bleaching-powder is such a mixture. The formation of bleaching-powder was explained by the simple formula

$$2Ca(OH)_2 + 4Cl = Ca(OCl)_2 + CaCl_2 + 2H_2O.$$

But this opinion was shaken by two facts which could not be long overlooked, viz.:—1st, that the presence of free calcium chloride in bleaching-powder is nothing like so clearly evidenced (by its deliquescence, solubility in alcohol, &c) as the above formula requires; and, 2nd, that the formula does not explain the notorious fact that solid bleaching-powder is not obtainable without a large quantity of free calcium hydrate. This caused a number of other

formulæ to be propounded. Fresenius (Ann. Chem. Pharm. cxviii. p. 317) asserted, on the strength of experiments made by F. Rose, that 4 molecules of calcium hydrate (according to modern notation) only absorbed 4 atoms of chlorine; in this process calcium hypochlorite and calcium oxychloride were formed, upon which chlorine does not act. Bleaching-powder results from this reaction:

$$4\,Ca(OH)_2 + 4Cl = Ca(OCl)_2 + CaCl_2, 2\,CaO + 4H_2O.$$

But this opinion is quite untenable; Bolley found (Chem. Centralblatt, 1859, p. 601) that calcium oxychloride

$$(CaCl_2, 2\,CaO + 16\,H_2O),$$

which is easily obtainable in a crystallized state, is certainly attacked by chlorine with formation of calcium hypochlorite; moreover, according to Fresenius's formula, bleaching-powder could not exist with more than 32 per cent. of bleaching chlorine, whilst every year in England about 100,000 tons of bleaching-powder are sold, guaranteed to contain 35 per cent. of available chlorine in the cask, and often in the fresh state containing upwards of 39 per cent. There is nothing left but to condemn as faulty the original experiments of F. Rose.

Millon and Muspratt assumed bleaching-powder to be a peroxide in which half of the oxygen is replaced by chlorine, $Ca\langle{}^{O}_{Cl_2}$; Martens takes it for a compound corresponding to chlorine hydrate in which hydrogen is replaced by lime, $(CaO)Cl_2$.

Quite impossible is the formula of Crace Calvert (Ann. Chim. Phys. [4] xxvii. p. 21), viz. $Ca(OCl_2) + 2CaCl_2$, founded upon inaccurate experiments and ultimately upon a wrongly constructed equation,

$$3\,Ca(OH)_2 + 6\,Cl = Ca(OCl)_2 + 2\,CaCl_2 + 3\,H_2O,$$

in which one oxygen is missing on the right side! Moreover Kolb (Compt. Rend. lxxv. p. 380) has proved Calvert's analytical methods to be quite misleading.

The formula of Odling ('Handbook of Chemistry,' German edition, i. p. 59) seems nearer the truth than the preceding ones. According to him, bleaching-powder is calcium chloride in which one atom of chlorine is replaced by the radical of hydrochlorous acid,

viz. $Ca\langle{}^{Cl}_{OCl}$. This opinion was founded upon the fact that bleaching-powder is not deliquescent [but *strong* bleach is so] and that alcohol does not dissolve any calcium chloride from it. It also explains the slight stability of this compound, which on contact with water instantly splits up into $CaCl_2$ and $Ca(OCl)_2$; and it would indeed leave hardly any thing to be desired if it accounted for the inevitable presence of an excess of lime in bleach; this, however, it does not do.

All the more recent researches* on the constitution of bleaching-powder (which have now to be mentioned) turn to a great extent upon the question why no bleach can be made without such an excess of calcium hydrate. The following are the views of Kolb (Compt. Rend. lxv. p. 530). Dry bleach, as rich in chlorine as it can be obtained (chlorure de chaux type), shows 123° Gay-Lussac = 38·72 per cent. of available chlorine, exactly corresponding to the old formula

$$2(CaO, HO, Cl) + CaO, HO,$$

which in modern notation would be

$$2\,CaOCl_2, H_2O + Ca(OH)_2.$$

[This formula cannot be correct, for this reason to begin with, that bleach with more than 38·72 per cent. of available chlorine can without any difficulty be obtained.] By water dry bleach is split up into insoluble calcium hydrate and a soluble portion in which $CaOCl_2$ or a multiple of it is contained; but at any rate, Balard states, it is split up into $Ca(OCl)_2$ and $CaCl_2$, because a concentrated solution of bleach contains an excess of $CaCl_2$. [The excess of $CaCl_2$, always contained in bleach over and above that required by the formula, alone causes this phenomenon, which by itself proves nothing.] Bleach-liquor is accordingly in any case a mixture of calcium hypochlorite and chloride; but probably the compound $CaOCl_2$ [or $Ca_2O_2Cl_4$] is only split up on contact with water; for perfectly dry carbonic acid and perfectly dry bleaching-powder behave thus, $2\,CaOCl_2 + 2\,CO_2 = 2\,CaCO_3 + 4\,Cl$; whilst $CO_2$ acts on damp or liquid bleach in this way,

$$[Ca(OCl)_2 + CaCl_2] + CO_2 + H_2O = CaCO_3 + CaCl_2 + 2\,HOCl;$$

so that a totally different grouping of atoms must exist here [this is controverted by Richter and Juncker, see below].

* The author's comments are generally given in brackets [ ].

In the above-quoted paper, in which Kolb proved the futility of Calvert's research, he showed that good bleach contains only a slight excess of calcium chloride (about equal to 1·2 per cent. chlorine) over the quantity necessary to form

$$CaOCl_2 \text{ or } Ca_2OCl_2 + CaCl_2.$$

Davis (Chem. News, xxvii. p. 225) made a few laboratory experiments in this direction. He made use of a chamber consisting of a leaden table standing over strong oil of vitriol and covered by a lid dipping into the latter. On the leaden table a ½-inch layer of slaked lime of the following composition was spread:—

| | |
|---|---|
| CaOH | 94·471 |
| $CaCO_3$ | 0·836 |
| $Al_2O_3$ | 0·629 |
| $Fe_2O_3$ | 0·159 |
| $H_2O$ (by diff.) | 3·531 |
| Insoluble | 0·374 |

The chlorine was dried by calcium chloride and oil of vitriol, and the following bleaching-powder made with it:—

| | |
|---|---|
| Available chlorine | 39·760 |
| Total chlorine | 39·760 [?] |
| Insoluble | 0·218 |
| Carbonic acid | 1·340 |
| Ferric oxide and alumina | 0·500 |
| Water (by difference) | 15·062 |
| Calcium oxide (total) | 43·120 |
| Do. (soluble) | 31·622 |
| Do. (combined with $CO_2$) | 3·389 |
| Do. (as hydrate) | 8·000 |

From these data Davis calculates the composition of that bleaching-powder as follows:—

| | |
|---|---|
| Hydrated calcium chloroxide ($CaOCl_2, H_2O$) | 81·200 |
| Calcium hydrate | 13·287 |
| ,, carbonate | 3·046 |
| Water (by difference) | 1·749 |
| Ferric oxide and alumina | 0·500 |
| Insoluble | 0·218 |
| | 100·000 |

From the same bleaching-powder, by continued action of dry chlorine a product containing 42·851 total chlorine, 39·051 available chlorine, and 11·492 water (inclusive of that of the hydrates) was obtained; by the action of more chlorine in the moist state, a product with 44·73 total and 37·87 available chlorine; by the simultaneous action of chlorine and $CO_2$ upon the last product, 38·342 total, 35·710 available chlorine, 3·313 carbonic acid. By the action of moist chlorine on calcium hydrate which was not luted by oil of vitriol, but by dilute sulphuric acid, he obtained a product with 35·556 total and 33·333 available chlorine; he thus found, in contradiction to Goepner, but in unison with practical experience, that moist chlorine does not yield such strong bleach as dry. In spite of all endeavours, Davis never succeeded in saturating the hydrated lime in bleaching-powder with chlorine; and he thinks that this fact should be accounted for in the formula.

In *Bleach-liquor* of spec. grav. 1·13, on the other hand, Davis found the lime almost saturated, viz.:—

| | |
|---|---|
| Calcium chloroxide | 13·524 |
| ,, chloride | 0·166 |
| Lime | 0·392 |
| Manganese | traces |
| Water (by difference) | 84·918 |
| | 100·000 |

He further gives a number of estimations of total and available chlorine in good and bad bleach; the excess of the former over the latter in good bleach is from 0·54 to 3·41, in bad bleach 1·06 to to 5·89 per cent. Bleach made by Deacon's process showed:—

| | I. | II. | III. |
|---|---|---|---|
| Total chlorine | 37·78 | 34·93 | 39·74 |
| Available chlorine | 29·72 | 31·42 | 31·57 |

He also found that the latter decomposes very quickly and falls *e. g.* from 27 to 20 per cent.

Göpner (Dingl. Journ. ccix. p. 204) assigns to bleaching-powder the simple formula $CaOCl_2$, and explains it as produced by a simple addition of chlorine to lime. [This could not be easily reconciled with our present notions of structural chemistry.] Calcium chloride is not present in the bleaching-compound, but is formed by

other causes:—partly by the assistance of $CO_2$, as chlorine acts upon calcium carbonate thus, $CaCO_3+4Cl=CaCl_2+ClOCl+CO_2$; but chiefly by the HCl never absent on the large scale. The calcium chloride arising in this way, as water for dissolving it is absent, forms crusts, which protect a good deal of hydrated lime from the action of chlorine. The hypochlorous acid is consequently not the bleaching compound of the bleaching-powder; and the assertion frequently made, that hypochlorous acid can be prepared by treating that compound with dilute mineral acids and distilling, Goepner declares to be erroneous. In the distillate only chlorine can be detected by Wolters's reaction. This consists in shaking with mercury—which with chlorine-water only yields white protochloride, but with hypochlorous acid an insoluble crystalline brown compound containing Hg, O, and Cl, whilst a little $HgCl_2$ enters into solution. Moreover, with $CO_2$ bleaching-powder yields no hypochlorous acid, but chlorine alone; it is only after long treatment of filtered bleach-solution with $CO_2$ that noticeable quantities of HOCl are found. The peculiar smell of bleach in the air is not (as hitherto generally assumed) the odour of hypochlorous acid, but that of chlorine, specifically changed by extreme dilution with air. [We shall see at the end of Chapter III. that neither of these assumptions can be correct.] For the manufacture of bleaching-powder a larger quantity of water than the 8 per cent. "usually present" is favourable; when Goepner passed chlorine through water at 60° or 70° C. and allowed it to act upon calcium hydrate, he obtained a product with 42·84 per cent. of available chlorine [?], the theoretical maximum for the formula $CaOCl_2$ being 55·9 per cent. [The last statement of Göpner's is contradicted by the generally known fact that with moist chlorine, at least on the large scale, no strong bleach can be obtained, and by Davis's special experiments (Chem. News, xxvii. p. 227), whilst on the small scale several observers have found the same thing (comp. below). In any case the assertion that usually 8 per cent. of water are present in the calcium hydrate employed in factories is decidedly wrong; frequently only 3 or 4 per cent. of water, or even less, are found in it.]

These statements and opinions of Göpner have been controverted in various quarters. First, Schorlemmer (Deutsche chem. Ges. Ber. vi. 1509) stated that the experiment of preparing hypochlorous acid from bleaching-powder had been made hundreds of times, and that he had himself, on distilling bleach-solutions with

dilute nitric or sulphuric acid, always obtained distillates which showed Wolters's reaction on ClOH. Göpner (ib. vii. p. 270) asserted that with fresh bleach and sulphuric acid that reaction is not obtained; but Schorlemmer (ib. p. 682) asserted positively that it is obtained; so that, according to him, the presence of hypochlorite is proved at least in the *solution* yielded by bleaching-powder. [The author has often repeated the same experiment as Schorlemmer, and with the same success.] Again, Frederking (Chem. Centralbl. 1876, p. 429) on repeating Göpner's experiments found HOCl, but no chlorine; he proved this both by Wolters's reaction and by pure gold leaf, which is acted upon by chlorine but not by hypochlorous acid.

Richter and Juncker (Dingl. Journ. ccxi. p. 31), in their examination of bleaching-powder, arrived at the following results, which contradict both those of Kolb and those of Göpner in several points. Dry bleach having the composition of Kolb's "chlorure de chaux type" they found (contrary to Kolb) as good as undecomposable by $CO_2$; when moistened with water, it yields on treatment with $CO_2$ both chlorine and hypochlorous acid (which contradicts Kolb, Göpner, and Hurter; see below). On employing sulphuric acid they always obtained chlorine exclusively, as hypochlorous acid. In order to decide the question, they employed phosphoric acid for decomposing (dry) bleach, and then also found in the distillate chlorine only: in the residue they found only 2·99 per cent. $CaCl_2$, which must have been present as an accidental admixture; for if the compound $Ca(OCl)_2 + CaCl_2$ had preexisted, at least 27·04 per cent. $CaCl_2$ ought to have been found in the residue. By this Richter and Juncker consider it decided that in *dry* bleaching-powder a compound of chlorine with calcium and oxygen must be assumed to be present, but not the mixture supposed by Balard and Gay-Lussac. It is another question whether that mixture is present in a *solution* of bleach or not; from their experiments they draw the same conclusion as all previous inquirers (except Göpner), viz. that on contact with water the bleaching-compound is split up into calcium chloride and hypochlorite. The $CaCl_2$ in bleach, apart from the cause stated by Göpner, viz. the action of $CO_2$ and HCl, is especially due to a splitting-up of $Ca(OCl)_2$ into calcium chloride and chlorate, produced by an excess of chlorine. They are decidedly opposed to Göpner's opinion, that the never failing excess of calcium hydrate in bleach is owing to a mechanical

protective action of calcium chloride, its amount being much too small for that. They connect the phenomenon with the observation made by Graham, and confirmed by Tschigianjang, Fricke, and Reimer (Dingl. Journ. cxcii. p. 297), according to which perfectly dry calcium hydrate does not absorb any chlorine; and by the $CaCl_2$ formed, but especially by the hygroscopical compound $CaOCl_2$, at a certain limit the calcium hydrate is deprived of the absorbed water and is thus made incapable of absorbing more chlorine.

To an attack made by Knapp (Dingl. Journ. ccxi. p. 461) Richter and Juncker replied (ib. ccxii. p. 339) without much advancing the matter. But much valuable experimental material is contained in the long memoir of Wolters (Journ. f. prakt. Chemie [2], x. p. 128), from which we will only extract his conclusions. Wolters had shown, like Richter and Juncker, that in decomposing bleach by acids chlorine and hypochlorous acid are always given off at the same time, but that the proportion of their quantities is very much influenced by the kind of acid employed. It is therefore probable that the argumentation hitherto employed, deducing the chemical constitution of bleach from the products of its decomposition by acids, is erroneous, the bodies set free by the acids being too quickly changed. Further experiments on the influence of chlorine on calcium sulphate, carbonate, &c., in which a formation of hypochlorous acid was proved, furnished the demonstration that under these circumstances the reaction is sufficiently energetic to explain the occurrence of the considerable quantities of hypochlorous acid which had been found on decomposing bleach. Owing to this reaction of chlorine on the salts of the alkalies and alkaline earths, and that of hypochlorous acid itself upon hypochlorides, the chemical constitution of bleaching-powder cannot be explained by decomposing it with acids. In further experiments Wolters made the important observation that chloride of lime and chloride of potash or soda behave differently: on being heated, the former yields chlorine, the latter yield none; nor are these acted upon by carbonic acid so strongly as chloride of lime. If this diversity in behaviour was caused by alkaline bleach-liquor containing $KOCl$, while bleaching-powder contained $CaOCl_2$, it was probable that hypochlorous acid, which, Wolters had noticed, was able to expel $CO_2$ from its salts [comp. the former contrary statements, p. 86], liberated chlorine from bleach according to this formula—

$$CaOCl_2 + Cl_2O = Ca(OCl)_2 + 2\,Cl.$$

But if bleach contains only calcium hypochlorite, the influence of hypochlorous acid could only cause an evolution of chlorine when its oxygen was employed for forming chlorous or chloric acid. When therefore Wolters brought together hypochlorous acid and bleach in dilute solutions, avoiding heating (the ClOH produces calcium chlorite and chlorate but very slowly from the cold dilute bleach solution), it could be recognized, from what took place, that the compound $CaOCl_2$ exists also in a *solution* of bleach; for in this case the presence of the greater portion of the free chlorine required by the above formula could in fact be proved. When, therefore, Wolters and Göpner in opposition to all previous observers, insist upon assuming that both liquid and solid bleach contain $CaOCl_2$ but no hypochlorite, this refers only to *fresh* solutions. In the course of time the presence of free chlorine, of calcium carbonate, phosphate, &c. in a solution of bleach converts a compound easily attacked by $CO_2$ into one acted upon by $CO_2$ only with difficulty, and that probably in the following manner. From $CaOCl_2$ the $CO_2$ of the air liberates chlorine, which acts upon calcium carbonate, forming $CaCl_2$, HOCl, and $CO_2$; and the two last again act upon $CaOCl_2$. These processes may be expressed thus:—

$$(1)\quad CO_2 + CaOCl_2 = CaCO_3 + Cl_2;$$
$$(2)\quad 4\,Cl + CaCO_3 = CaCl_2 + CO_2 + Cl_2O;$$
$$(3)\quad Cl_2O + CaOCl_2 = Ca(OCl)_2 + 2Cl.$$

If free chlorine and calcium sulphate or phosphate &c. be present, or if the chlorine be liberated by sulphuric or phosphoric acid, the reaction

$$(4)\quad 4\,Cl + CaSO_4 + H_2O = H_2SO_4 + CaCl_2 + Cl_2O$$

follows, and upon this again the reaction no. 3. The final result of all these processes is that $CaOCl_2$ is converted into calcium hypochlorite $Ca(OCl)_2$. Touching the question why so large a quantity of free lime occurs in solid bleach, whilst in bleach-liquor the lime can be made to vanish almost entirely, Wolters contradicts the opinion of Richter and Juncker, that this is caused by the hygroscopicity of calcium chloride and chloroxide; but he does not unconditionally adopt the opinion of Goepner, that the quicklime is protected by a covering of calcium chloride; Wolters, like Bolley, infers that the protective action of the formed $CaOCl_2$ itself comes into play. Wolters's process for estimating hypochlorous acid along with chlorine and chlorous and chloric acids is described in Journ. f. prakt. Chemie [2], vii. p. 468, and Dingl. Journ. ccx. p. 362.

The next examination of this matter we owe to Opl (Dingl. Journ. ccxv. pp. 233 and 325). He also is of opinion that both in solid bleaching-powder and in its solution the compound $CaOCl_2$ is contained. By preparing bleach containing 38·7 per cent. Cl, 30·52 CaO combined, 21·33 CaO free, and 9·45 $H_2O$, he proved that the bleaching-compound cannot possibly have the composition assigned to it by Kolb, viz. $CaOCl_2, H_2O$ (which requires more water), and that consequently it is not a hydrate. If the attempt is made to deprive bleach of more water, *e. g.* by $CaCl_2$, free chlorine is given off; with a decreasing percentage of $H_2O$ that of CaO rises. If bleach is to be made with only a small quantity of free $Ca(OH)_2$, much water must be present. [This agrees with many other observations *up to a certain limit*; beyond this the bleach becomes lumpy and absorbs no more chlorine till sufficient water to form bleach-liquor is added; we shall see at the end of this Chapter that the strongest *dry* bleach is made with a very small quantity of free water in the calcium hydrate.] It appears that the compound $CaOCl_2$ cannot exist by itself—that for its stability a certain quantity of water is required, though not in atomic proportions, and that the less the free calcium hydrate present the more water is required. The sum of the quantities of lime and water which render the compound $CaOCl_2$ stable increases with the temperature; bleach made at a higher temperature is consequently weaker; but a definite law cannot be established for this. Opl estimates the different chlorine compounds thus:—To a normal solution of arsenious acid a certain quantity of the bleach solution is added, in which case only the chlorine of the compound $CaOCl_2$ acts upon $As_2O_3$. Now a solution of indigo of known strength is run in till it is no more decolorized by chlorous acid; then the remainder of undecomposed arsenious acid is titrated back by a good bleach-liquor of known strength. The total chlorine and the total chloric acid are estimated in a second sample, after destroying all chlorine oxides except chloric acid by boiling with ammonia, so that on titrating with silver nitrate all the chlorine is estimated except that of chloric acid; by evaporating and igniting the residue the total chlorine is found.

Limpach (Chem. Centralbl. 1876, p. 257) comes essentially to Wolters's opinions, and consequently adopts Odling's formula $Ca\langle^{Cl}_{OCl}$.

The research of Kopfer (Ann. Chem. Pharm. clxxvii. p. 314) principally combats Wolters's opinions. His results are as follows:—If to a filtered bleach-solution or to dry bleach so much of a dilute mineral acid is added that the free lime is saturated and the hypochlorite present on Gay-Lussac's hypothesis is decomposed, and if the mixture is distilled, the distillate is an aqueous solution of nearly pure $Cl_2O$, which in the most favourable case amounts to 92 per cent. of the $Cl_2O$ corresponding to the hypochlorite. From this it follows that bleaching-powder is either calcium hypochlorite or a compound having the constitution $Ca\begin{smallmatrix}\diagup OCl \\ \diagdown Cl\end{smallmatrix}$. Either hypothesis explains the occurrence of hypochlorous acid under the above circumstances equally well; and both lead to a plausible theory of the formation of bleaching-powder by the action of chlorine on calcium hydrate. At first one atom of chlorine replaces one of the hydroxyls in $Ca(OH)_2$; the latter, on the moment of formation, combines with the hydrogen of the second hydroxyl to form water, whilst this atom of hydrogen is replaced by a second atom of chlorine. This explains why chlorine is not absorbed by quicklime, which cannot be understood on the assumption that chlorine is directly combined with CaO; for from a special analysis it appears that the compound $CaOCl_2$, if it exists at all, must be anhydrous. Kopfer objects to Wolters's assumption that mineral acids always liberate at first chlorine from bleach, and that hypochlorous acid only occurs as a secondary formation; for if so much acid is added to bleach that the lime is saturated and all hypochlorite is decomposed, no chlorine at all is obtained, but merely hypochlorous acid, and on shaking this mixture with mercury brown oxychloride is formed, by which the presence of hypochlorous acid is demonstrated. Hence the latter may be more simply explained as a direct product of the decomposition of bleaching-powder by mineral acids, which can only be done by either Gay-Lussac's or Odling's formula. But that the former should be preferred, is proved by Kingzett's crystallized calcium hypochlorite. [Not at all! The latter compound, supposing it to be indisputably composed as assumed, may be explained most easily as a secondary formation in the bleach-solution.] The quantitative methods employed by Wolters are declared by Kopfer to be quite worthless. Wolters on this part (*ib.* clxxix. p. 246) rejects Kopfer's method of investigation as incorrect, and again expresses the opinion that distilling-

experiments with acids cannot give any clue as to the constitution of bleaching-powder; since the results are always explainable by either hypothesis. [This indeed cannot be denied, and it must be confessed that the mass of observations accumulated during the last few years, chiefly as the first work of young chemists, and extremely contradictory to each other, has left us pretty much at the same point of ignorance regarding the constitution of bleaching-powder.]

Some essential progress in this direction was claimed to be made by Stahlschmidt (Deutsch. chem. Ges. Ber. viii. p. 869; more explicitly, Dingl. Journ. ccxxi. pp. 243, 335). He explains the formation of bleaching-powder by the formula

$$3Ca(OH)_2 + 4Cl = 2CaHClO_2 + CaCl_2 + 2H_2O.$$

The bleaching-compound is explained as calcium hydrate in which one atom of hydrogen is replaced by chlorine: $Ca\begin{smallmatrix}\diagup OH\\ \diagdown ClO\end{smallmatrix}$. When this comes into contact with water, it splits up into $Ca(OCl)_2$ and $Ca(OH)_2$. This hypothesis would certainly explain very well the unavoidable presence of lime in bleaching-powder, which had been left very much in the dark by the previous investigations. Stahlschmidt's results are, in detail, as follows:—In contradiction to some previous observations he established the fact that even absolutely dry calcium hydrate yields bleaching-powder, nay, even (as Kopfer also had found) calcium hydrate mixed with quicklime, in proportion to its percentage of hydrate. [The author can confirm this.] A lower temperature under these circumstances retards the formation of bleach; this is still more influenced by trifling circumstances in preparing the hydrate. Calcium hydrate dried at 100° C. is less active than that dried over oil of vitriol; slowly slaking quicklime is less adapted for bleach-making than quickly slaking lime, &c. If the operation is properly conducted, the chlorine admitted slowly, and the absorbing-vessel kept cool, all the chlorine is obtained as available chlorine; but when the gas is admitted too quickly, in which case the mass becomes heated, the available chlorine amounts to several per cent. less than the total chlorine. In three experiments he obtained, from 100 calcium hydrate, 163·99 bleaching-powder with 39·06 per cent. available (39·02 per cent. total) chlorine, 164·9 bleach with with 38·91 per cent. available (39·37 per cent. total) chlorine, and

164·28 bleach with 38·85 per cent. available (39·12 total) chlorine. His formula, as above, would yield 163·96 bleach with 39·01 per cent. available chlorine, which agrees very well with these results. In a few rare cases more than 39·01 per cent. available chlorine was obtained, in one case 40·59 per cent. Göpner also mentions having obtained, by means of chlorine passed through warm water, bleach with 40·02 and 42·84 per cent. available chlorine. [Hurter (Dingl. Journ. ccxxiii. p. 77) also says that good Weldon bleach contains about 1·5 per cent. $CO_2$ and a little silica, and yet can be got up to 40 per cent. oxidizing chlorine, which militates against a formula admitting only 39 per cent. chlorine; we shall see below that this is true beyond contradiction.] Stahlschmidt explains this in the following way:—Pure dry bleach is decomposed by water, forming calcium hypochlorite and hydrate; and the latter with more chlorine forms bleach again, according to the above formula. On employing moist chlorine a portion of the compound $2CaHClO_2$ can thus be decomposed into $CaCl_2O_2$ and $CaO_2H_2$, and the latter immediately transformed into $CaHClO_2$. The two molecules of water becoming free in this reaction, which are especially retained by the calcium chloride, may serve for the above decomposition; and ultimately, according to the formula

$$2Ca(OH)_2 + 4Cl = Ca(OCl)_2 + CaCl_2 + 2H_2O,$$

a mixture of equal molecules of calcium hypochlorite and chloride would be obtained, which, after deducting the water taken up from the moist chlorine, would contain 48·96 per cent. of available chlorine. Up to this point it is possible to go theoretically [in practice this can only be done in the case of bleach-liquor.] In the bleaching-powder manufactured on the large scale, which is made from hydrate of lime containing an excess of 8 per cent. [?] of water, real calcium hypochlorite occurs in varying quantities, probably along with $CaHClCO_2$.

The theoretical limit for $Ca(ClO)_2 + CaCl_2$ would be obtained by adding chlorine-water to calcium hydrate suspended in water. For this reason, and on account of the statements of Schorlemmer, Kopfer, and Kingzett, Stahlschmidt adopts the view that solution of bleach contains calcium hypochlorite. He also confirms the disputed statement of Kolb that damp bleach is decomposed by $CO_2$ with liberation of hypochlorous acid, from experience gained in manufacturing bleach by Deacon's process on the large scale.

He opposes the view that in bleach a compound $CaO+Cl_2$ is contained; Göpner's and Wolters's experiment he regards as refuted by Schorlemmer and Kopfer; Richter's and Juncker's phosphoric-acid process is also inconclusive, since that acid itself decomposes $CaCl_2$ and liberates HCl. Göpner's theory, according to which, say, 0·483 gram calcium chloride "envelops" about 25 grams calcium hydrate and protects it from being converted into bleach, is unintelligible and impossible; Richter's and Juncker's theory, that the excess of water required for producing bleach is absorbed by the compound $CaOCl_2$ itself in consequence of its hygroscopic property, is completely refuted by his own and Kopfer's experiment, according to which even a mixture of quicklime and dry calcium hydrate yields bleach; hence no such excess of water is at all necessary. With Kolb Stahlschmidt agrees so far, that 3 molecules of calcium hydrate and 4 molecules of chlorine react upon each other; but they differ as to the existence or the state of combination of calcium hydrate and chloride. Stahlschmidt's bleach with 39 per cent. available chlorine was, as stated, formed exactly according to the formula

$$3\,CaO_2H_2 + 4\,Cl;$$

the percentage of caustic lime, which consequently might theoretically amount to 15·38, was actually from 15·29 to 15·67; the chlorine of the $CaCl_2$ arising according to his equation should be 30·49, and was actually found to be 29·88 to 30·74 per cent. (It was estimated by adding $SO_2$, by which $CaSO_4$ is formed and all the chlorine of the $CaHClO_2$ must pass into HCl, which is driven off by heating, so that only the chlorine of the $CaCl_2$ remains.) Hence every thing agrees with the formula

$$CaHClO_2 + CaCl_2 + 2H_2O.$$

The 2 molec. water can be driven off at a comparatively low temperature (found 9·41 to 10·01, instead of 9·89 per cent); the third molec. water contained in the original calcium hydrate is not liberated even at a red heat, at which both calcium hydrate and calcium chloride easily and quickly part with their water; hence it must form an essential ingredient of bleach. But all three molecules of water can be driven off by heating with soda—calcium carbonate, sodium chloride, and free oxygen being formed. At a higher temperature bleach also loses chlorine, viz.:—at 120° C.,

4·6 per cent.; on heating in a bulb-tube over the lamp, 10·85 and 11·60 per cent.; together with water and oxygen. The processes going on in this case are not yet explained; but it is certain that at a higher temperature, when bleaching-powder melts to a readily fusible clear glass, a compound is formed which still contains hydrogen. This, as well as the fact that precisely one third of the lime is prevented from forming bleach, militates against Göpner's formula.

Stahlschmidt's opinion that strong bleach contains neither free lime nor calcium oxychloride, seems to be confirmed by the investigation of Salzer (Dingl. Journ. ccxxx. p. 418).

Unfortunately even Stahlschmidt's investigation did not finally settle the question of the constitution of bleaching-powder. He also assumed the occurrence of calcium chloride as a necessary link in the process of producing bleach; and according to his formula bleaching-powder

$$(2\,CaHClO_2 + CaCl_2 + 2\,H_2O)$$

would contain 30·49 per cent. free $CaCl_2$, with 19·5 per cent. chlorine. Hence this theory would become impossible if it were proved that bleaching-powder is completely or for the most part decomposed by $CO_2$; for nobody will dispute that $CaCl_2$ cannot be decomposed by $CO_2$—a reaction which would falsify every organic analysis by combustion, if it took place in reality. This has been asserted to be a fact by several previous observers. It has certainly been disputed; but quite recently it has been again confirmed by Parnell, and especially by a very competent and in this respect unbiassed observer, viz. Hurter (Dingl. Journ. ccxxiii. p. 428), on the strength of positive experiments. In Hurter's experiments bleach decomposed by $CO_2$ only showed 1·5 per cent. oxidizing chlorine, along with 4·25 or 4·6 or 6·0 per cent. chlorine as chlorate and the chloride necessarily formed along with it, and only another 5·0 or 0·7 or 0·39 per cent. chlorine as calcium chloride independent of the former. The formation of chlorate is easily explained by the well-known fact that, when free chlorine acts upon moist calcium carbonate, much hypochlorous acid is formed, which is quickly transformed into chloric acid; hence much chlorate is always found in bleach containing much carbonic acid, but none in good bleach. From these facts and from his observations that weak bleach (27 to 29 per cent.) when brought to a red heat loses next to no chlo-

rine, and that on heating strong bleach 27 to 28 per cent. chlorine always remain, Hurter concludes that bleaching-powder is a peculiar compound, in which no calcium chloride occurs as such.

In view of the numerous contradictions among the above summed-up researches, not merely concerning points of theory, but actual matters of fact which should admit of a final decision by experiment, the author set one of his pupils, Mr. Schäppi, to reinvestigate the more important points in dispute. The following is a summary of the results, obtained under the author's own eyes; the details of the experiments will be published hereafter.

I. *Influence of Water on the preparation of bleaching-powder.*—The experiments were made by exposing the lime to the action of chlorine in glass dishes standing on a leaden table with double rim; the annular space between the two rims was filled with sulphuric acid of spec. gravity 1·4 (at which strength it neither gives out nor absorbs moisture at ordinary temperature); and a glass bell-jar dipping below into this hydraulic lute formed the sides and roof of the chlorine-chamber. The chlorine was introduced through a neck on the top of the bell-jar by a tube reaching about halfway down, whilst another tube, beginning just underneath the india-rubber cork, gave exit to the air and the excess of the gas. The lime employed was extremely pure, and contained only about 0·5 per cent. $CO_2$. In the following statements the water is to be understood to comprise that of hydration as well; and it should be remembered that pure $Ca(OH)_2$ corresponds to 24·32 per cent. $H_2O$, but the lime employed could only hold about 23·5 per cent. as water of hydration.

(a) *Chlorine completely dried by strong sulphuric acid* yielded with

| Lime containing of $H_2O$ | Bleaching-powder containing of available chlorine |
|---|---|
| 6·5 per cent. | 9·06 per cent. |
| 13·6 „ | 32·86 „ |
| 13·64 „ | 33·34 „ |
| 17·6 „ | 37·38 „ |
| 17·6 „ | 37·64 „ |
| 21·6 „ | 38·82 „ |
| 24·0 „ | 40·71 „ |
| 26·0 „ | 40·89 „ |
| 27·8 „ | 43·13 „ |
| 27·8 „ | 43·42 „ |
| 28·2 „ | 40·36 „ |
| 30·1 „ | 38·78 „ |
| 31·8 „ | 36·85 „ |

Another series of 5 examples, chlorinated at the same time under the same jar (so that probably the sample containing most water yielded some of it to the drier ones) showed :—

| Lime containing of $H_2O$ | Bleach containing of available chlorine |
|---|---|
| 6·5 per cent. | 12·49 per cent. |
| 13·6 „ | 35·38 „ |
| 21·6 „ | 40·18 „ |
| 24·0 „ | 43·09 „ |
| 41·0 „ | 20·34 „ |

(b) *Chlorine not dried by sulphuric acid, but deprived of most of its moisture by passing it through a 40-inch tube filled with pumice* (which would approach the condition of the gas as evolved in factories and passed through a long series of pipes), yielded, with

Lime containing 24 per cent. $H_2O$, bleach containing 42·12 per cent. available Cl.
„ „ 26 „ „ „ 41·59 „ „
„ „ 28·2 „ „ „ 40·54 „ „

(c) *Chlorine washed with water of* 15° C., *not dried at all:*

Lime with 20 per cent. $H_2O$ = bleach with 34·47 per cent. available Cl.
„ 24 „ = „ 41·76 „ „
„ 26 „ = „ 40·71 „ „

(d) *Chlorine passed through water at 40° C.*:

| | | | | | | |
|---|---|---|---|---|---|---|
| Lime of | 24·0 per cent. | $HO_2$ | = bleach of | 38·26 | per cent. | available Cl. |
| „ | 24·0 | „ | = „ | 38·24 | „ | „ |
| „ | 26·0 | „ | = „ | 39·31 | „ | „ |

(e) *Chlorine passed through water at 75–80° C.*:

| | | | | | | |
|---|---|---|---|---|---|---|
| Lime of | 24·0 per cent. | $H_2O$ | = bleach of | 37·0 | per cent. | available Cl. |
| „ | 25·3 | „ | = „ | 38·43 | „ | „ |
| „ | 26·0 | „ | = „ | 38·96 | „ | „ |

(The bleach obtained was no longer in the state of dry powder, but lumpy and damp.)

(f) *Lime dried on the water-bath, to expel all excess of water,* containing 24·0 per cent. $H_2O$, treated at the same time with lime of 25·3 per cent. $H_2O$:

| | With completely dried chlorine. | Chlorine roughly dried by pumice. |
|---|---|---|
| Lime of 24 per cent. $HO_2$ = | bleach of 39·3 | 41·59 per cent. Cl. |
| „ 25·3 „ = | „ 40·6 | 40·6 „ |

These experiments decide the following points:—

1st. It is not true that dry calcium hydrate does not absorb chlorine, and that a proportion of uncombined water is necessary for this reaction; on the contrary, completely dry $Ca(OH)_2$ absorbs very much chlorine even in the presence of very much free CaO.

2nd. *Dry* chlorine acts decidedly better than moist gas, even when the latter has been freed from HCl by washing; but drying mechanically and no doubt incompletely by a 40-inch course of pumice serves nearly as well as drying completely by sulphuric acid.

3rd. The strongest bleach seems to be obtained when about 4 per cent. $H_2O$ are present along with $Ca(OH)_2$; but these 4 per cent. may be furnished either by an excess of water in the lime itself, or by the moisture of imperfectly dried chlorine with lime containing only the water theoretically necessary for hydration. Since on the large scale the chlorine is never perfectly dried, the latter condition of the lime would seem to be most favourable.

4th. Passing the chlorine through warm water does not in any case increase the strength of the bleach, but the contrary.

5th. The strongest bleach obtainable in those experiments was 43½-per-cent.; and several times this figure was approached; con-

sequently no formula of bleaching-powder can hold good which demands less bleaching chlorine than 43 per cent.

II. *Treatment of bleaching-powder with Air.*—

(a) *Air saturated with moisture*, passed over bleach of 43·09 per cent., caused no evolution of gas at 60° C.; but the evolution set in at 80° C., and was completed a little above this. The escaping gas contained merely oxygen, no chlorine; the residue showed 39·42 per cent. Cl as chloride and 2·99 per cent. as chlorate. The latter would retain oxygen corresponding to 14·95 per cent. Cl as $CaOCl_2$; and the oxygen actually given off must have proceeded from a splitting-up of $CaOCl_2$ into $CaCl_2$ and O.

(b) *Dry air*, passed over similar bleach for 44 hours. Here the escaping gas contained no sensible quantity of oxygen, but some chlorine (4·73 per cent. of the bleach); the residue contained Cl 3·99 per cent. as chloride, 0·23 as chlorate, 34·78 as available (bleaching) chlorine.

(c) *Dry air*, passed over bleach of 42·7 per cent. for 6 hours at 100–105° C. The escaping gas contained both chlorine and oxygen, viz. 0·87 per cent. of the bleach O (corresponding to Cl 6·86 per per cent. as $CaOCl_2$) and 14·94 per cent. as Cl; the residue contained Cl 22·25 per cent. as chloride, 3·51 as chlorate, 1·35 as bleaching chlorine.

These experiments prove the following points.

1st. *Moist air* at about 80° C. causes the bleaching-compound to give up oxygen—all the chlorine being retained, partly as chloride, partly as chlorate. The following reactions take place:—

$$(1)\quad CaOCl_2 = CaCl_2 + O;$$
$$(2)\quad 6\,CaOCl_2 = Ca(ClO_3)_2 + 5\,CaCl_2.$$

2nd. *Dry air* at about 100° C., besides yielding the same products as moist air, also causes a direct splitting-up of the bleaching-compound into lime and chlorine, thus:—

$$(3)\quad CaOCl_2 = CaO + Cl_2.$$

III. *Treatment of bleaching-powder with Carbonic Acid.*—

(a) *Dry*, $CO_2$ *passed at ordinary temperatures* over bleach of 43·09 per cent. for many days in succession, yielded a very little chlorine (or HOCl) at first only, apparently as long as any moisture was present; then the action ceased, and most of the available chlorine was found again in the residue.

(b) *Dry* $CO_2$ *at higher temperatures* yielded the following results:—

| | Laboratory bleach, 43·09 per cent. | English bleach, 34 per cent. (originally 39 per cent.). | | Swiss bleach, 34 per cent. | English bleach, 34 per cent. | | | |
|---|---|---|---|---|---|---|---|---|
| | 40 minutes at 95–100° C. | 1 hour at 100° C. | 2¼ hours at 70–75° C. | 2 hours at 60°, then ½ hour at 100° C. | 3¼ hours at 55–60° C. | 2 hours at 70°. | 2 hours at 70°. | 2 hours at 70°. |
| Chlorine escaped as gas | 34·20 | 28·28 | 30·48 | 29·75 | 25·3 | 29·21 | 28·41 | 27·50 |
| Chlorine in residue as bleaching Cl | 1·31 | 2·47 | 0·84 | 0·58 | | | | |
| " " chloride | 6·14 | 5·67 | 4·98 | 3·45 | | | | |
| " " chlorate | 1·00 | 2·09 | 0·74 | 0·89 | | | | |

(c) *Dry* $CO_2$ *with bleaching-powder completely dried over sulphuric acid* produced no change whatever when cold; at 80° C., 2·66 chlorine per cent. were given off, at a higher temperature much oxygen but no chlorine, evidently from the action of the heat alone.

(d) *Moist* $CO_2$ liberated from English bleach (34 per cent.) at 70° C., in one hour, 29·58 per cent. chlorine.

(e) *Calcium chloride,* treated with $CO_2$ at 70° C., exactly like the bleach in the preceding experiments, yielded no chlorine at all, as might have been expected.

These experiments seem to prove conclusively *that no formula of bleaching-powder is correct which admits the presence of calcium chloride,* since in the presence of a little moisture nearly all the chlorine is expelled by carbonic acid at about 70° C. The small quantity of chlorine remaining as chloride in the residue can be easily accounted for by the formation of a little chlorate, which was actually proved to be present. That the action is very slight in the absence of all moisture, cannot be a matter of surprise; but even the presence of very much moisture would not explain how $CaCl_2$ could be decomposed by $CO_2$ with liberation of chlorine. Hence the formulæ of Gay-Lussac, Kolb, Stahlschmidt, &c., all become impossible, whilst Odling's formula $Ca^{Cl}_{OCl}$ is quite compatible with all the preceding experiments, and seems to be the real formula of the bleaching-compound.

IV. *Behaviour of the Water contained in bleaching-powder.*— On heating different samples of strong bleach to the fritting point, in six experiments (along with 5·41–9·39 per cent. Cl) 14·60–18·09 $H_2O$ escaped, estimated by absorption in $CaCl_2$. Another sample, which at first lost 17·56 per cent. $H_2O$, on being heated with sodium carbonate lost 2·98 more $H_2O$, total 20·54; but from another portion of the same bleach 20·08 per cent. $H_2O$ could be expelled by heating up to the fusing-point, without any sodium carbonate. A third portion of the same sample lost, when heated to 150° C., 14·21; from 150° to 200° C., 0·29; from 200° to 290° C., 1·12; from 290° to red heat, 5·35; total 20·97 per cent. water. A number of other experiments with bleaching-powder from various sources yielded similar results: namely, the greater portion of the water was expelled below 150° C., the remainder only above 290° C., but by heat only, without the necessity of adding sodium car-

bonate. This disproves Stahlschmidt's conclusion, that the formula of bleach comprises hydroxyl, which cannot be expelled as water by mere heating up to fusion, but only by the aid of $Na_2CO_3$.

The facts just ascertained are explained by an experiment with lime containing 31·5 per cent. $H_2O$. Of this there were expelled, below 150° C. 9·33, from 150° to 290° 0·80, from 290° to a red heat 21·34 per cent. Since there was a little calcium carbonate and silica present, the water expelled from 290° up to red heat equals almost exactly that corresponding to $Ca(OH)_2 = CaO + H_2O$, whilst practically all the mechanically absorbed water was expelled below 150° C. From this it seems to follow that the 4 or 5 per cent. of water remaining in bleaching-powder up to 290° C. are mostly due to calcium hydrate present in the free state, whilst the water expelled at lower temperatures may be partly due to a hydrate of the bleaching-compound $CaOCl_2$, partly to mechanical (hygroscopical) absorption. A portion of the latter (7 to 8 per cent. of the bleach) is lost on keeping the bleach in an exsiccator over strong vitriol. The strongest bleach contained then less than one molecule $H_2O$ to one of $CaOCl_2$, apart from the water corresponding to $Ca(OH)_2$. A complete analysis of the strongest bleach showed present :—

| | |
|---|---|
| $CaOCl_2$ | 77·05 |
| $CaCO_3$ | 0·96 |
| $CaCl_2$ | 0·45 |
| $Ca(OH)_2$ | 6·74 |
| Water* (by diff.) | 14·80 |
| | 100·00 |

The small quantity of calcium present as hydrate (being only $\frac{1}{7}$ of that present as $CaOCl_2$) does not seem to call for any elaborate attempts at explanation by formulæ, but can be accounted for without difficulty as being mechanically protected from the attack of chlorine by the large bulk of the bleaching-compound $CaOCl_2$. Possibly the latter may be to some extent protected from decomposition by the excess of calcium hydrate, which takes up the $CO_2$ of the atmosphere; but it really does not seem necessary to alter Odling's formula on that account.

* N.B. The actual estimation of water nearly agreed with this analysis, viz. within 0·66 per cent.

# CHAPTER II.

## THE MANUFACTURE OF CHLORINE.

At first chlorine was always made from manganese, common salt, and sulphuric acid, which act as follows:—

$$MnO_2 + 2NaCl + 2SO_4H_2 = MnSO_4 + Na_2SO_4 + 2Cl + 2H_2O.$$

Hence a residue is obtained which is a mixture of sodium and manganese sulphate very difficult to utilize. But in the infancy of alkali-making the high price of soda permitted the working of these residual liquors for it, *e.g.* at St. Rollox about the year 1800 (Mactear, *l. c.*). This mode of preparing chlorine is nowadays practised only in laboratories, and in some isolated cases where gaseous chlorine is used for bleaching, and where the difficulty of transit renders the salt and sulphuric acid cheaper than their equivalent of hydrochloric acid. This happens, for instance, at some paper-mills, but becomes more and more rare.

As soon as by the development of alkali-making larger quantities of *hydrochloric acid* became available, this acid was at once made use of; and it is now the only source for the bleaching-powder, bleach-liquor, and chlorate of lime of commerce.

Many processes have been proposed for liberating the chlorine of HCl, which we shall briefly notice later on; but (excepting Deacon's process, which will also be described hereafter) all chlorine is nowadays made, as by its discoverer Scheele, from *peroxide of manganese* or other of the higher manganese oxides, of late mostly from the $MnO_2$ recovered by Weldon's process—which, however, is always originally derived from native manganese-ore

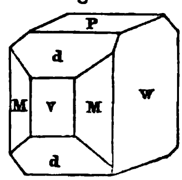
and must be continually made up from the same. The reaction is this:

$$MnO_2+4HCl=MnCl_2+2H_2O+2Cl.$$

The so-called *manganese-ore* is pure only exceptionally, being mostly a mixture of several of the following ores with each other or with gangue:—

*Pyrolusite*$=MnO_2$ with 63·6 Mn and 36·4 O. It crystallizes in rhombic prisms—M, fig. 38, forming an angle of 93° 40′ with the longitudinal face *w* and the transverse face *v*, ending in the horizontal prism *d*=140° and the straight end face P. The crystals occur in the columnar, acicular, and tabular forms. Mostly, however, the mineral is indistinctly crystalline in aggregates of different shapes with a radiating and fibrous structure; these also occur in pseudomorphs after calcspar, brown manganese-ore, and polianite. It is cleavable along the prisms P, the faces *w* and *v*. Its hardness is only 2·0 to 2·5; the finely fibrous varieties are still softer. Specific gravity 4·7 to 5·0; colour dark steel-grey to light iron-grey. Fracture black, soils the fingers; lustre half-metallic. On heating yields only oxygen, no water. This ore, the best of all, is found *passim* in many places; in larger quantities at Elgersburg and Ilmenau in Thuringia, in Devonshire, in the Spanish province of Huelva, in New Zealand, in New Caledonia (Chem. News, xii. p. 234), in the State of Virginia and elsewhere in the United States. A variety of this ore, identical with it in chemical composition, is *polianite*, which is distinguished from it by its form of crystallization and its hardness (6·5 to 7).

Fig. 38.




The following are analyses of pyrolusite (from Richardson and Watts's Chem. Technol. iii. p. 345):

| | Turner, from Devonshire. | Turner, from Elgersburg. | Turner, from Thlefeld. | Scheffler, from Ilmenau. | Arfvedson, from Undenaes. | Dufrenoy, from Tarn. | Riegel, from Krettnich. |
|---|---|---|---|---|---|---|---|
| $Mn_3O_4$ ........ | 85·617 | 84·05 | 85·62 | 77·0 | 83·56 | 72·5 | 86·00 |
| O ........ | 11·599 | 11·78 | 11·60 | 11·6 | 14·58 | 9·8 | 11·45 |
| $Fe_2O_3$........ | ...... | ...... | ...... | 1·3 | ...... | 14·2 | 0·40 |
| $Al_2O_3$ ........ | ...... | ...... | ...... | 0·3 | ...... | ...... | ...... |
| BaO ........ | 0·665 | 0·53 | 0·66 | 1·2 | ...... | ...... | ...... |
| CaO ........ | ...... | ...... | ...... | 0·3 | ...... | ...... | ...... |
| $SiO_2$ ........ | 0·553 | 0·51 | 0·55 | 0·8 | ...... | 1·4 | 0·71 |
| $H_2O$ ........ | 1·566 | 1·12 | 1·57 | 5·8 | 1·86 | 1·6 | 1·40 |
| | 100·000 | 97·99 | 100·00 | 98·3 | 100·00 | 99·5 | 99·96 |

*Braunite,* $Mn_2O_3$, with 70 Mn and 30 O, is distinguished from pyrolusite above all by its great hardness, which exceeds that of felspar (6·0 to 6·5). It crystallizes in tetragonal octahedra of 109° 53′ with straight end face &c., but usually very indistinctly, in granular aggregations. Spec. grav. 4·8 to 4·9. Iron-black or brownish black; does not soil the fingers; fracture black, with a metallic fatty lustre. Is mostly found along with pyrolusite. Analyses according to Richardson and Watts :—

| | From Elgersburg (Turner). | From Tellermark. (Tonsager). | From Elba (Bechi). | From Vizianagram in India (Scott). | From Marceline (Damour). |
|---|---|---|---|---|---|
| MnO ......... | 86·94 | ...... | 88·31 | ...... | 19·17 |
| $Mn_3O_4$ ...... | ...... | 86·40 | ...... | ...... | ...... |
| $MnO_2$......... | ...... | ...... | ...... | 73·79 ? | 67·37 |
| O ............ | 9·85 | ...... | 3·08 | 1·86 | ...... |
| $Fe_2O_3$......... | ...... | 1·57 | 4·75 | 12·91 | 1·45 |
| BaO ......... | 2·26 | ...... | 1·03 | ...... | ...... |
| CaO ......... | ...... | ...... | ...... | ...... | 1·22 |
| MgO ......... | ...... | ...... | ...... | 2·34 | ...... |
| $SiO_2$ ......... | trace | 9·84 | 0·75 | 8·30 | 10·43 |
| $H_2O$ ......... | 0·95 | 1·98 | 2·08 | 0·54 | ...... |
| | 100·00 | 99·79 | 100 00 | 99·74 | 99·64 |

*Brown manganese-ore* (*manganite*), $Mn_2O_3, 2H_2O$, =62·6 Mn, 27·2 O, 10·2 $H_2O$. Vertical rhombic prisms, often in bundles or druses and twin crystals, also in fibrous microcrystalline aggregations. Hardness 3·5 to 4, spec. grav. 4·3 to 4·4; colour dark steel-grey up to iron-black; fracture brown. Imperfectly metallic lustre. Found in veins in the porphyry at Ihlefeld, Ilmenau, Christiansand (Norway), and elsewhere, often with fluorspar, heavy spar, ferric oxide, &c. Varieties of it are *Varvicite* with only 5 or 6 per cent. water and some $MnO_2$ along with $Mn_2O_3$, and *Newkirksite.*

*Hausmannite,* $Mn_3O_4$, with 72·2 Mn and 27·8 O. Crystallized in the tetragonal system, often in twins, also microcrystalline. Hard-

ness 5 to 5·5; spec. grav. 4·7 to 4·8. Iron-black, fracture brown; strongly metallic lustre. Occurs along with the other manganese oxides, but is of very little value for chlorine-making.

| | Ihlefeld (Turner). | Ilmenau (Rammelsberg). |
|---|---|---|
| Red $Mn_2O_3$ ...... | 98·902 | 99·44 |
| O.................... | 0·215 | 0·05 |
| BaO .............. | 0·111 | 0·15 |
| $SiO_2$ .............. | 0·337 | ...... |
| $H_2O$ ......... ..... | 0·435 | ...... |
| | 100·000 | 99·64 |

*Psilomelane,* is cryptocrystalline, mostly in botryoidal, kidney-shaped, and other forms, with a smooth or rough surface, mostly of shelly structure, rarely fibrous. Fracture shelly to plain. Hardness 5·5 to 6; spec. grav. 4·1 to 4·2. Colour iron- or blue-black; fracture brownish black and lustrous, otherwise dull. Frequently found in Cornwall, Devonshire, Ihlefeld, Ilmenau, Siegen, Spain, North America, &c. Its composition is usually complicated; along with $MnO_2$ there occur MnO, BaO, and $K_2O$, also other metals; it is uncertain whether only mechanically mixed or chemically combined. It contains mostly 4 or 6 per cent. water. Its powder imparts a red colour to concentrated sulphuric acid (Analyses, p. 118).

*Wad* is similar in its chemical composition to psilomelane, but does not form a distinct mineralogical species; it is probably the product of decomposition of other manganese-ores; it occurs in compact, bulbous, botryoidal, often scaly or earthy form, and always with much water. It is very soft and mild, soils the fingers, is very light and porous, even floating on water, and hence very easily acted upon by hydrochloric acid. Spec. grav. 2·3 to 3·7. Brown to brownish black, dull or faintly lustrous. Found at Elbingerode in the Harz, in Franconia, in the Siegen district, in Nassau, Devonshire, Derbyshire, New York, at Vicdessos and Groroi in France (groroilite), in Sweden, &c. It is a very important manganese-ore (Analyses, p. 119).

| | From Schneeberg (Turner). | From Romanèche (Turner). | From Horhausen (Rammelsberg). | From Baireuth (Fuchs). | From Ilmenau (Scheffler). | From Thiviers (Berthier). | From Elgersburg (Herter). | From Gy, Haute Saône (Ebelmen). | From Heidelberg (Rammelsberg). | From Ilmenau (Clausbruch). | From Langneberg (Heyl). | From Skidberg, Sweden (Bahr). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Mn_3O_4$ ... | 69·80 | 70·97 | 81·36 | 81·8 | 73·3 | 64·10 | ...... | ...... | ...... | ...... | ...... | ...... |
| MnO ...... | ...... | ...... | ...... | ...... | ...... | ...... | 74·61 | 70·60 | 70·17 | 77·23 | 68·00 | 64·64 |
| O........... | 7·36 | 7·26 | 9·18 | 9·5 | 9·8 | 7·50 | 16·06 | 14·18 | 15·16 | 15·82 | 13·62 | 17·16 |
| $Fe_2O_3$...... | ...... | ...... | 1·43 | ...... | 0·3 | 6·80 | ...... | 0·77 | ...... | ...... | ...... | ...... |
| $Cu_2O$ ...... | ...... | ...... | 0·96 | ...... | ...... | ...... | 0·46 | ...... | 0·30 | 0·40 | 0·36 | ...... |
| CoO ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 0·54 | ...... | ...... | 0·03 |
| $Al_2O_3$...... | ...... | ...... | ...... | ...... | 2·1 | ...... | ...... | ...... | ...... | ...... | ...... | ...... |
| CaO ...... | ...... | ...... | 0·38 | ...... | 1·8 | ...... | 1·84 | ...... | 0·60 | 0·91 | 0·20 | 0·61 |
| MgO ...... | ...... | ...... | 0·32 | ...... | ...... | ...... | 0·64 | 1·05 | 0·21 | ...... | 0·53 | 0·29 |
| BaO ...... | 16·36 | 16·69 | ...... | ...... | 5·8 | 4·60 | 2·40 | 6·55 | 8·08 | 0·12 | 8·59 | 16·04 |
| $K_2O$ ...... | ...... | ...... | 3·04 | 4·5 | ...... | ...... | 0·92 | 4·05 | 2·62 | 5·29 | 0·27 | 0·29 |
| $SiO_2$ ...... | 0·26 | 0·95 | 0·53 | ...... | 1·7 | 10·00 | ...... | 0·60 | 0·90 | 0·52 | 2·18 | ...... |
| $H_2O$ ...... | 6·22 | 4·13 | 3·39 | 4·2 | 4·3 | 7·00 | 2·70 | 1·67 | 1·42 | ...... | 3·95 | ...... |
| | 100·00 | 100·00 | 100·59 | 100·0 | 99·1 | 100·00 | 99·63 | 99·47 | 100·00 | 100·29 | 97·70 | 99·06 |

| | From Clausthal (Klaproth). | From Devonshire (Turner). | From Derbyshire (Turner). | From Viedessos (Berthier). | From Groroi (Berthier). | From Siegen (Berthier). | From Ilmenau (Scheffler). | From Rübeland (Rammelsberg). | From Gothland (Igelström). | From New York. (Beck). Hillsdale. | From New York. (Beck). Austerlitz. | From Skidberg (Bahr). | From Krummau (Kussin). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Mn_3O_4$ ... | 68·0 | 79·12 | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 66·16 | ...... |
| MnO ...... | ...... | ...... | ...... | 69·80 | 62·4 | 58·5 | 66·5 | 67·50 | ...... | ...... | ...... | ...... | 64·40 |
| $MnO_2$...... | ...... | ...... | 38·59 | ...... | ...... | ...... | ...... | ...... | 82·51 | 68·50 | 58·50 | ...... | ...... |
| O............ | ...... | 8·82 | ...... | 11·70 | 12·8 | 10·4 | 12·1 | 13·48 | ...... | ...... | ...... | ...... | 7·37 |
| $Fe_2O_3$...... | 6·5 | ...... | 52·34 | ...... | 6·0 | 5·7 | 1·0 | 1·01 | 0·77 | 16·75 | 22·00 | 2·70 | 11·12 |
| CuO ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... |
| CoO ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 0·02 | ...... |
| $Al_2O_3$*...... | ...... | ...... | ...... | 7·00 | ...... | 10·7 | ...... | ...... | 6·30 | ...... | ...... | 0·75 | ...... |
| BaO ...... | 1·0 | 1·40 | 5·40 | ...... | ...... | ...... | 8·1 | 0·36 | ...... | ...... | ...... | 15·34 | ...... |
| CaO ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 4·22 | 1·91 | ...... | ...... | 0·59 | ...... |
| MgO ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 0·69 | ...... | ...... | 0·28 | ...... |
| $K_2O$ ...... | ...... | ...... | ...... | ...... | ...... | ...... | ...... | 3·66 | ...... | ...... | ...... | 0·28 | ...... |
| $SiO_2$ &c.... | 8·0 | ...... | 2·74 | ...... | 3·0 | 1·8 | 2·5 | 0·47 | 1·43 | 3·25 | 2·50 | 0·92 | ...... |
| $H_2O$ ...... | 17·5 | 10·66 | 10·29 | 12·40 | 15·8 | 12·9 | 9·8 | 10·30 | 5·58 | 11·50 | 17·00 | 12·07 | 14·10 |
| | 101·0 | 100·00 | 109·36 | 100·90 | 100·0 | 100·0 | 100·0 | 101·00 | 99·19 | 100·00 | 100·00 | 99·11 | 96·99 |

The most important mines from which manganese was formerly supplied for technical purposes were those of Ilmenau and Elgersburg in Thuringia, Ihlefeld in the Harz, and Giessen in Hessia, then in the Nassau and Siegen country, and at Romanèche in France (Saône-et-Loire). These sources of ore have been put very much into the background by the much richer manganese-ore from the Spanish province of Huelva, from which in 1865 already 24,430 tons were exported. In the north of Spain also, at Aleria and Cavadonga, there are manganese-mines with ore containing on the average 70 per cent. $MnO_2$; but these are very little worked as yet. Other large beds of pure manganese-ore have been discovered in New Zealand, in Cuba, in several of the Southern States of North America, quite recently also in Westphalia and in the Italian alpine valleys of Aosta and Tournanche; but since the price of manganese has considerably receded in consequence of the general introduction of Weldon's recovery process, most of those beds do not pay for working.

The following Table shows the influence of Spanish manganese on the other mines :—

*Manganese-ore produced in the Duchy of Nassau.*

| | | | |
|---|---|---|---|
| In 1828, | 496 cwt. | 1857, | 670,192 cwt. |
| 1837, | 8,011 „ | 1858, | 463,502 „ |
| 1847, | 213,679 „ | 1859, | 349,887 „ |

In 1857, moreover, 225,474 cwt. were produced in other parts of Germany; but since that time the production has been very much restricted, owing to the competition of the superior Spanish ore.

The manganese-ore met with in trade is frequently much more impure than the analyses above given would show. Its *value for producing chlorine* of course depends first of all upon the oxygen present over and above that necessary to form MnO, because it is this only that evolves chlorine from muriatic acid. As a rule this is not expressed in parts per cent. of oxygen, but of manganese peroxide; *e.g.* pure manganese sesquioxide is calculated as if it were $MnO + MnO_2$, red manganese oxide as $2MnO + MnO_2$, &c. When it is stated that an ore contains 60 or 70 per cent. $MnO_2$, this only means that 100 parts of it liberate as much chlorine as 60 or 70 per cent. pure $MnO_2$ would do. But the presence of MnO

is not indifferent, since it consumes acid as well, and too large a percentage of it may make an ore, otherwise pure, worthless on account of consuming too much hydrochloric acid. Of the remaining constituents of ordinary manganese-ores, some are comparatively harmless, but others, such as ferric oxide and free alkalies or alkaline earths (or combinations of them with $MnO_2$) are injurious because they consume HCl, and FeO because it absorbs oxygen. Even the insoluble matters, like barium sulphate and silica, are frequently very injurious, because they mechanically obstruct the action of HCl; often in the chlorine-stills lumps of substances are found covered with silica, but consisting inside of unchanged manganese-ore. More injurious than any thing else are the carbonates of calcium &c., as they not only consume acid but give off $CO_2$, which exerts an extremely harmful influence in the manufacture of bleaching-powder. In England ores containing upwards of 1 per cent. $CO_2$ are not considered merchantable. Such ores can be almost completely deprived of the carbonates by crushing and treating with dilute acids or acid still-liquor; but this is always an expensive process.

The physical state of manganese-ore is also of importance for its value. Generally the soft descriptions are much superior to the hard ones, because they are more easily dissolved in the acid and require a smaller excess of it than the latter; there exist some ores of high strength but such hardness that they can only be dissolved by a great excess of acid and steam, and consequently have only a small value. All these things must be attended to when buying manganese. The *consumption of muriatic acid* is not usually estimated directly, but is felt in the following custom of the trade. The normal percentage for German manganese is 60 per cent. $MnO_2$ in the dry state; each 1 per cent. above or below that strength is paid for at a certain rate, usually 2*s*. per ton; nothing below 57 per cent. $MnO_2$ is accepted at all. For Spanish and similar ores the normal strength is 70 per cent., with a bonification of 2*s*. 6*d*. pro per cent. up or down, 65 per cent. being the minimum allowed. The price of 70-per-cent. manganese is much higher than if it were calculated on the basis of 60 per cent. The minimum of carbonic acid allowable is usually stated at 1 per cent., sometimes at ½ per cent.

### *The Valuation of Manganese Ore.*

This is usually restricted to the following points:—1st, the estimation of the moisture; 2nd, that of the $MnO_2$; 3rd, that of the $CO_2$. Regarding the *moisture* there is not perfect agreement. Fresenius pointed out that manganese loses its hygroscopic moisture at 100°C. very slowly and not quite completely, but at 120°C. completely; if that temperature is exceeded, the chemically combined water also begins to be expelled. Fresenius constructed a peculiar drying-apparatus for manganese, consisting of a thick cast-iron dish with a number of holes in which small numbered brass pans, containing the samples, are placed. In England the drying is always done at 100° C., which is against the seller, since the higher percentage of completely dry manganese-ore makes it much more valuable than in the simple ratio of the moisture lost. But then the extremely finely ground sample ought to be kept at 100° C. for at least six hours.

The estimation of *peroxide* can be made in very various ways, the most important of which we will now mention.

Gay-Lussac estimated the quantity of oxygen evolved from manganese by sulphuric acid according to the following equation:—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

3 grams of manganese are heated in a small retort with 25 cubic centims. of strong oil of vitriol; and the gas evolved is collected in a graduated tube over dilute caustic potash liquor, which absorbs any $CO_2$ present. 1 vol. of oxygen corresponds to 2 vols. of chlorine. This plan is rather tedious, not very accurate, and probably little employed now.

Fresenius and Will, according to a principle previously stated by Berthier and Thompson, estimate the $MnO_2$ by the oxidation of oxalic acid; the loss of weight caused by the escape of the $CO_2$ formed is the measure for the percentage of $MnO_2$. The reaction taking place is:—

$$MnO_2 + H_2SO_4 + C_2H_2O_4 = MnSO_4 + 2H_2O + 2CO_2.$$

Hence each 88 parts of $CO_2$ escaping correspond to 86 parts of $MnO_2$. (In England formerly the weight of $MnO_2$ was assumed = the $CO_2$ escaping, which yielded too high a result.) For this estimation either the original two-flask apparatus of Fresenius and

Will, or one of the many more novel apparatus for estimating carbonic acid by loss of weight is employed. Of the latter, which are lighter and more easily handled, those of Geissler and Mohr are the best known. But, of course, the escaping $CO_2$ may also be absorbed by soda, lime, or in a potash-bulb apparatus &c., and its weight found directly. Under all circumstances the water given off at the same time must be retained by calcium chloride or concentrated sulphuric acid; and the carbonic acid, already present in the ore as carbonates, must be estimated either by a parallel experiment without oxalic acid, or by weighing the apparatus first with the ore and the sulphuric acid separate, then again after mixing them and driving off the $CO_2$, and once more after adding a weighted quantity of oxalic acid and completing the decomposition. Of course, at the end of the operation air must be sucked through the apparatus, as the much higher specific gravity of carbonic acid gas would occasion a very perceptible error.

The process of Fresenius and Will was formerly the general one for the analysis of manganese-ores; but for some years past it has very much receded into the background—because it is not so convenient as Bunsen's or the iron process, requiring as it does two or three weighings of a heavy apparatus down to milligrams, and also because the harder descriptions of manganese, in spite of the finest grinding, can only be dissolved with the help of prolonged heating, almost inevitably causing some $CO_2$ to escape unabsorbed. It has also been reproached with not entirely oxidizing the magnetic iron oxide ($Fe_3O_4$) which frequently occurs in manganese-ores; this, however, is completely oxidized to $Fe_2O_3$ when the ore is employed for the production of chlorine. For this reason, in 1869 the English union of alkali-manufacturers altogether rejected the Fresenius-Will process. Pattinson (Chem. News, xxi. p. 267) proved that reproach to be unfounded, as the lower oxides of iron in this process are always oxidized up to $Fe_2O_3$; but still he prefers the iron method, on account of its greater certainty in execution, especially with hard ores. In order to lessen the errors in the Fresenius-Will process, all cork joints must be covered with wax or paraffine, and the apparatus be allowed to cool *completely* and remain some time in the glass case of the balance before weighing.

Another way of employing the same reaction is to treat the ore with a known quantity of oxalic acid and retitrate the unused

portion of the latter. About 2 grams of extremely finely ground manganese are heated with 50 cubic centims. of normal oxalic-acid solution and 5 or 6 cubic centims. of strong sulphuric acid, till the completeness of the decomposition is indicated by the black colour of the sediment vanishing entirely; then, without filtration, after dilution with water, the liquid is re-titrated with standard permanganate solution at 60° C., till a pink colour appears: or only an aliquot portion of the liquid may be treated in this way. Each 90 parts of oxalic acid (calculated as anhydrous) thus indicated as destroyed correspond to 86 parts of $MnO_2$; for

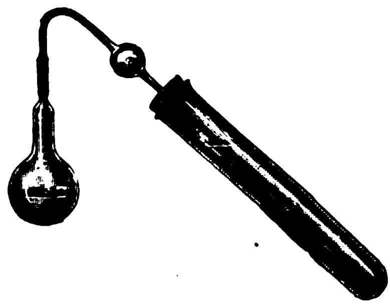
$$MnO_2 + C_2H_2O_4 = 2CO_2 + MnO + H_2O.$$

The results obtained by this process are very good (Paul, Chem. News, xxi. p. 16).

The process of Bunsen is the most suitable for the employment of manganese on the large scale, as it directly measures the chlorine produced by it. Yet it is not much employed in factories, because the results obtained by it do not always agree—probably not through any fault of the method, but of its manipulation. Certainly absolutely pure potassium iodide, free from iodate, should be employed; and even in this case the results are not always exact. The process of expelling the chlorine and receiving it in KI does not by itself yield such perfectly correct results as it is generally assumed to yield. Even if the KI and the hydrochloric acid employed are absolutely pure (*i. e.* on being mixed cold remain colourless for some time), some iodine will be set free if the acid be boiled for some time in Bunsen's apparatus and the steam condensed in a solution of potassium iodide, as in testing manganese it must be. Several drops of hyposulphite solution are required for decolorizing the KI solution; how many, should be discovered by a preliminary test with the same quantity of acid as afterwards employed in the manganese-test; and the quantity of hyposulphite thus required must be deducted from the final result. The apparatus shown in fig. 39 is very convenient for Bunsen's test. The neck of the small flask is drawn out so as to be easily connected by an elastic joint with the gas-pipe; the latter is fitted loosely by a cork into a large test-tube containing the iodide solution, and the test tube kept cool by immersing it in a beaker filled with cold water. At the end of the operation the gas-pipe,

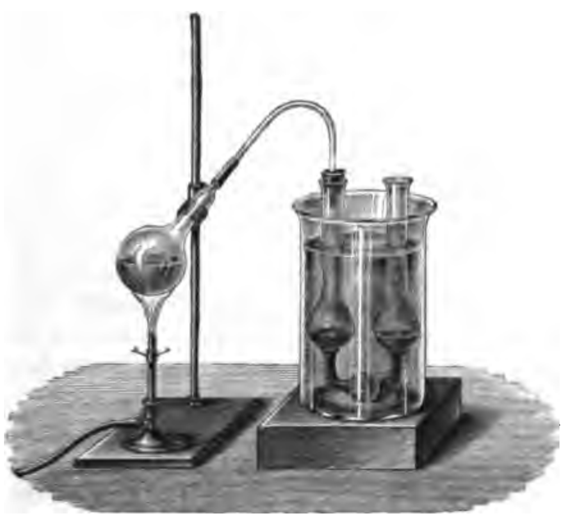
with the flask still attached to it, must be quickly drawn out of the solution, before the boiling has ceased and the liquor has had

Fig. 39.



time to come back beyond the bulb blown in the pipe. With the apparatus in the shape represented in fig. 40 there is no danger of any liquor coming back at all; but it is safer to employ a second

Fig. 40.



receiver filled with KI solution, which need not be emptied if no iodine has been liberated in it.

In all these cases about 0·3 gram manganese are put into the flask, which must hold 50 or 60 cub. centims.; about 25 cub. centims. of pure fuming hydrochloric acid are added, and the neck of the flask at once connected with the gas-pipe. The receiver has been previously charged with 25 or 30 cub. centims. of concentrated potassium-iodide solution, which must be kept cool during the operation by an external surrounding of cold water. The evolution of chlorine commences directly the flask is moderately heated; the current of chlorine should not be too strong, lest any escape unabsorbed; at last the liquid must be strongly boiled in order to drive over all the chlorine along with the steam and HCl. It is still safer to arrange the apparatus so that a current of air can be drawn through it during the operation, to expel all the chlorine. When the liquid in the flask has become of a clear light yellow colour, the lamp is removed, and with the apparatus fig. 39 the gas-pipe is taken out of the receiver as well; but with the apparatus fig. 40 no special precaution is necessary. If on removing the gas-pipe from the flask there is a smell of chlorine perceptible in the latter, the experiment must be rejected. The chlorine driven over liberates its exact equivalent of iodine in the KI solution; and this can be measured either by sodium hyposulphite or by sodium arsenite, as we shall see later on when treating of chlorometry. According to the equation

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl,$$

each 86 parts $MnO_2$ correspond to 71 chlorine or 253·7 iodine; or $5 \times 0·086$ ($=0·430$) gram would take up 100 cub. centims. of a decinormal iodine solution; hence, if 0·430 gram of manganese-ore are employed for each test, the number of cub. centims. of decinormal hyposulphite or arsenite solution required for decolorizing the liberated iodine indicates immediately the percentage of $MnO_2$. The titration should take place at once, since after long standing the HI liberated by the HCl carried over is decomposed with separation of iodine.

If sodium arsenite be employed for retitration, the acid reaction of the liquid must be taken away, *e.g.* by adding ammonium carbonate. Sodium hyposulphite should not be employed at a temperature above 20°, as otherwise some sulphate will be formed

along with tetrathionate (Wright, Chem. News, xxi. p. 103). According to Pickering (Journ. Chem. Soc. xxxvii. p. 128) a little sulphate is formed even at the ordinary temperature; but this seems quite immaterial, as the standard of the hyposulphite solution is ascertained with pure iodine or in some other manner under the same circumstances.

The most usual process of testing manganese-ores, at least in England, is that proposed by Levol and Poggiale, by means of iron. It is based upon the principle employed by Pelouze in estimating nitric acid (Vol. I. p. 54), viz. upon the oxidation of ferrous into ferric salt by the higher oxides of manganese, and remeasuring the unused ferrous salt. The manganese-ore is dissolved in the presence of a certain quantity of a ferrous salt or of metallic iron, and hydrochloric or sulphuric acid, and titrated back by potassium bichromate or permanganate. The substances formerly employed, ferrous sulphate precipitated by alcohol, or Mohr's ammonio-ferrous sulphate, cannot be recommended for this process, because they do not afford any absolute certainty of composition; hence the finest soft-iron wire (called flower wire) is preferred, which may be assumed = 99·7-per-cent. iron, and which is best analyzed once for all. Of this a known quantity is dissolved in the flask represented in fig. 3 (Vol. I. p. 55), preferably in sulphuric acid, both because ferrous sulphate in an acid solution is much more stable than ferrous chloride, and because on titrating with permanganate in the presence of HCl some chlorine is always given off. This solution is employed for standardizing the potassium-permanganate solution. Then again the same quantity of iron wire is dissolved; a weighed quantity of finely ground manganese-ore is added, the liquid boiled again, and retitrated after cooling, exactly in the same way as before. Much less permanganate will now be required; and from the difference the $MnO_2$ is easily calculated, since 56 iron answer to 43 $MnO_2$. It is best to dissolve $\frac{1}{2}$ gram of iron wire in 100 grams of dilute sulphuric acid (1 part $SO_4H_2$ to 3 parts $H_2O$), and then to add $\frac{1}{2}$ gram of manganese-ore. If several tests have to be made in succession, it is much quicker work to prepare a solution of ferrous sulphate in 20 parts of water, add $\frac{1}{2}$ part of oil of vitriol, and take (with a pipette) equal portions of it for standardizing by means of permanganate and dissolving the manganese. The permanganate must itself be standardized in another way, preferably by iron wire.

Instead of the dissolving-flask having an india-rubber valve, the neck of the flask may be closed by a cork through which passes a twice-bent glass tube, one limb of which ends just below the cork, whilst the other, much longer limb dips into a beaker filled with water. If any traces of chlorine should be liberated by particles of manganese carried to the surface, without acting upon the iron solution, they would be absorbed in the water outside; this, on removal of the flame, comes back into the flask, and its chlorine still acts upon the iron.

The *carbonic acid* in manganese-ore is estimated in the way mentioned in connexion with Fresenius and Will's method. In the case of small quantities (about 1 per cent.) this plan, owing to the slightness of the difference of weight, is not sufficiently exact. It is then best to absorb the gas in ammonia, precipitate $CaCO_3$ by means of $CaCl_2$, and estimate the former alkalimetrically. Traces of carbonic acid are discovered if the ground ore is stirred with water in a watch-glass till the adhering air is removed, then a little dilute HCl added, and the surface of the liquor looked at sideways; any $CO_2$ appears as minute gas-bubbles which cannot be confounded with air-bubbles.

*The quantity of hydrochloric acid required for dissolving the manganese-ore* is sometimes estimated, as it is very different for the same quantity of $MnO_2$ indicated by the test, if the composition of the ore varies. If, for example, the analysis indicates 60 per cent. $MnO_2$, this might all be present as real manganese dioxide, along with 40 per cent. gangue, and would require much less HCl than if, along with 60 per cent. $MnO_2$, 40 per cent. of MnO were present. These are both extremes which do not happen in practice; and on the whole practical wants are satisfied by the above-mentioned custom of the trade, according to which the ore is not paid for in direct proportion to its percentage of $MnO_2$, but on a much higher scale; for a rich ore nearly always consumes comparatively less acid than a poor one. The oxides of manganese behave towards hydrochloric acid as follows:—

$$MnO + 2HCl = MnCl_2 + H_2O;$$
$$Mn_3O_4 + 8HCl = 3MnCl_2 + 4H_2O + 2Cl;$$
$$Mn_2O_3 + 6HCl = 2MnCl_2 + 3H_2O + 2Cl;$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + 2Cl.$$

Besides, any iron oxides occurring in the ore consume acid without yielding chlorine, not to mention carbonates.

Still the quantity of HCl required for decomposing the manganese-ore ought to be estimated much more frequently than it usually is. This is done by dissolving a certain weight of ore in a known quantity of hydrochloric acid, in a flask with a reflux-cooler, or, more simply, fitted with a vertical glass tube, 3 feet long, passing through its cork, so that any HCl volatilized by the heating is condensed and runs back into the flask, whilst the chlorine may escape. When the decomposition is quite complete, the flask is allowed to cool, its contents are diluted, and the remainder of the acid titrated back. This can be done by Kieffer's cuprammonium-sulphate, prepared by carefully adding ammonia to a solution of cupric sulphate till the precipitate of $Cu(OH)_2$ formed at first is almost completely dissolved again. The liquid is filtered, and its value estimated by running standard hydrochloric or sulphuric acid from a burette into 10 cubic. centims. of it till a lasting precipitate has appeared. With this solution the acid manganese solution is titrated exactly up to the same point; and thus the free acid of the latter, and consequently that expended in dissolving, is found. It is, however, much easier to employ as an indicator the ferric oxide which is always present in manganese-ores, and simply to add standard soda or ammonia to the acid manganese solution till reddish brown flakes of ferric hydroxide are formed, which on shaking do not redissolve. Also tropæoline might be employed as an indicator for free acid, as mentioned in Vol. I. pp. 45, 47.

### *The Chlorine-stills.*

We have already seen that during the first period of manufacturing bleaching-powder, when hydrochloric acid was not yet cheap enough, chlorine used to be made from common salt, manganese, and sulphuric acid. If these materials are mixed in the proportions indicated by theory, *i. e.*

$$MnO_2 + 2NaCl + 2SO_4H_2,$$

a very high temperature must be employed in decomposing them, as at first monosodium sulphate ($NaHSO_4$) is formed and only half the chlorine is liberated; hence the heat must be increased beyond 120° C. (which is not easily done in practice by means of steam),

or more sulphuric acid must be employed, according to the equation

$$MnO_2 + 2NaCl + 3SO_4H_2 = MnSO_4 + 2NaHSO_4 + 2H_2O + 2Cl.$$

This, again, makes the manufacture of chlorine more expensive. The latter proportion would mean 87 $MnO_2$, 117 NaCl, and 297 $SO_4H_2$, and yield 71 chlorine; but as the materials are not pure, about 1 part of common salt, 1 part of ground manganese, and 2½ parts of vitriol are taken, the latter previously diluted with an equal weight of water, or employed in the state of chamber-acid.

For preparing chlorine from salt and sulphuric acid, leaden apparatus were usually employed (represented in fig. 41). The

Fig. 41.


principal part is a leaden still; the lower portion cf this is surrounded by an iron jacket B B separated by a narrow interval from the still-sides, so that the latter can be heated by steam entering through the pipe H. Sometimes the lower portion of the still was arranged for heating by direct fire, by constructing it as a cast-iron dish with a rabbet in its upper edge, into which the leaden upper part was cemented. The latter is provided with the charging-hole D for manganese, the funnel-tube C for muriatic acid, the gas-pipe P for chlorine, and the opening E for the vertical shaft of the agitator J. All openings are provided with water-lutes (as indicated), which must be deep enough to prevent any escape of gas at the

highest pressure experienced by friction on the pipes or other resistances. Such water-lutes are regularly employed in chlorine-making, because most other joints do not stand, owing to the rapid destruction of screw-bolts &c. The pipe G serves for running off the contents of the still at the end of the operation.

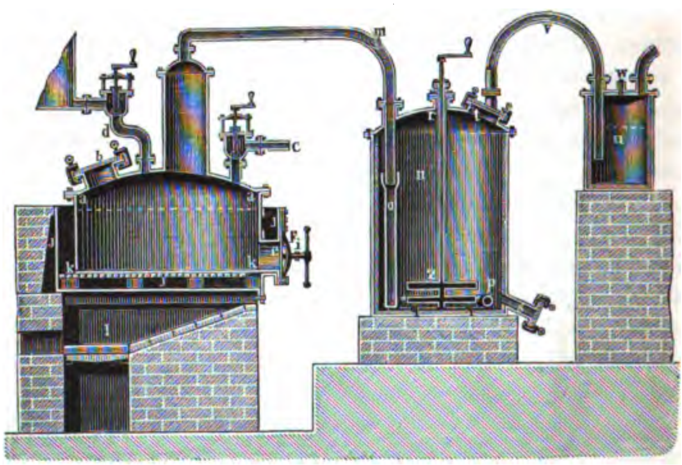
Apparently, for some decades such leaden stills were exclusively in use, although very often needing repair and quickly worn out. For liquid hydrochloric acid they cannot be used at all, because when heated it quickly dissolves the lead. On Dec. 28, 1828, Morfit patented, as an improvement, lining the leaden retorts with glazed stoneware. Gamble's was a much more important improvement (patent, March 14, 1839). He abandoned the use of lead, except for the lid, and employed deep stoneware pots with a jacket enclosing an annular space 3 inches thick, in which there was a circulation of hot water, hot solutions of salt, or steam. The pot tapered towards the bottom, where it had a discharge-pipe; it was again contracted at the top, so that the lead of the cover could be turned over it and tightened by an iron hoop; between lead and stoneware oil cement was put. These stills were each provided with an agitator, and accordingly could be employed for ground manganese, salt, and sulphuric acid, or for manganese and muriatic acid, as the lead cover only came into contact with gaseous HCl.

The stoneware apparatus to be described below might also be employed for making chlorine gas from salt and sulphuric acid; but if no agitators are provided, the materials must be well ground and mixed together.

The residue from this operation (a mixed solution of manganous and sodium sulphate) is almost worthless; and, as we have seen, this mode of operation is applicable now in rare cases only. The grinding of manganese is also expensive. On the large scale, for a long time past, hydrochloric acid and manganese have been used exclusively; but this cannot easily be done, except at sulphate-works, since the cost of packing and carrying muriatic acid is out of proportion to its value; hence the manufacture of bleaching-powder is only possible where the HCl itself is produced. A transition to this is afforded by the process of decomposing NaCl and $SO_4H_2$ in one compartment of a vessel, and allowing the gas to pass into the other compartment, where manganese is suspended in water. In this case the residue from the first compartment

might be used as acid sodium sulphate; but the decomposition is incomplete, and the apparatus impracticable. According to Wagner's Jahresb. 1857, p. 105, Clément is said to have proposed such an apparatus (when ?). Maughan (pat. March 22nd, 1836) was probably the first to act upon manganese directly with the HCl formed in the decomposition of common salt by sulphuric acid. The manganese, in fragments, was contained in a vertical cylinder provided with a grate just above the bottom, and was constantly kept moist by water. The cylinder was enclosed in a jacket in which steam circulated and kept the temperature up to at least 55° C. The HCl gas entered at the top; the chlorine passed out at the bottom; it was to be washed and then brought to a red heat in platinum tubes (!), and ultimately cooled and conveyed into the absorbing-chambers. A similar apparatus, patented by Seybel on March 31, 1842, is represented in fig. 42. *a a* is a leaden retort,

Fig. 42.



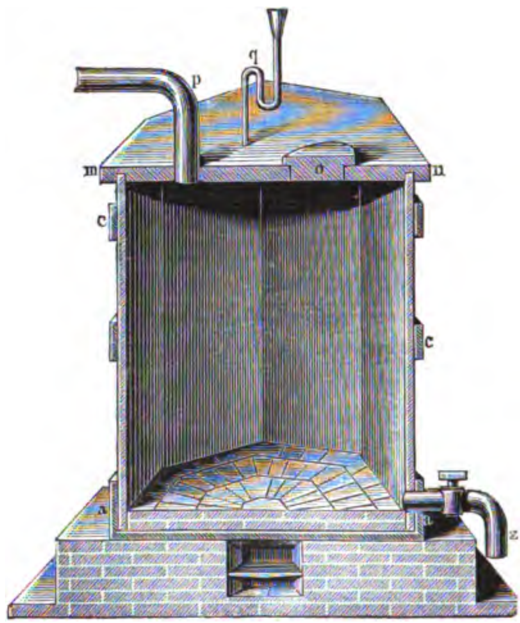
in which salt is decomposed by vitriol; *b* is the man-hole for charging the salt; *c*, a pipe, leading towards the chimney, closed by a valve during the decomposition; *d*, a pipe, with a valve, to admit the vitriol; *e*, discharging-pipe for the sodium bisulphate, covered by leaden lid F, held fast by an iron frame, screw-bolt, and arm *i*. J J is an iron oil-bath with a perforated false bottom *k k* as support for the vessel *a a*. The heat in *a a* was not to exceed

166° [? !]. The charge consisted of 1 ton of salt and $1\frac{1}{2}$ ton of sulphuric acid of spec. grav. 1·71. The HCl escapes through *m* into the manganese-vessel *n*, lined with firebricks. The pipe *m* is continued into a stoneware pipe *o*, and this into a hollow ring *p* with several small holes, through which the HCl gas is conducted below the level of the water and the manganese. The latter is from time to time stirred up by an iron agitator *z*, lined with lead, which passes through the gland *r*. *s* is the discharge-hole; *t*, manhole; *v*, gas-pipe. The chlorine is washed in *u* with water and about 5 kils. of manganese; the water can be siphoned off through *w*. *n* is charged with 7 cwt. manganese of 62 per cent. and 11 or 12 cwt. of water; it is worked off in 15 hours. The many practical difficulties of this apparatus are evident; it has hardly ever proceeded beyond the stage of trial.

The same principle was again patented by Monod (Sept. 13, 1856); he employed a manganese-vessel with a perforated false bottom. Baggs and Simpson once more patented the same thing (May 15, 1862).

The manufacture of chlorine from manganese and hydrochloric acid cannot be carried out very well except in vessels of stone or stoneware. At first these were often built as shown in fig. 43. They were composed of eight stone slabs, kept together by a cast-iron bottom piece with a flange *a*, midway and toward the top by hoops *c c*, and at the top by the stone cover *m n*. The bottom was paved with a double course of firebricks, as a protection against the acid. The hole *o* admitted the charge of manganese, *q* that of the acid; *p* carried off the chlorine gas; *z* was for the discharge of the waste liquor. A small fireplace beneath the iron bottom, as in the figure, or a steam-jacket served for the heating. These apparatus are said to have sometimes exploded—which, however, cannot have been a consequence of their construction, and may happen with any construction through an excess of pressure. Neither are the joints more difficult to keep tight than others; but probably the iron bottom was not sufficiently protected from the acid by the brick pavement; and the heating of the apparatus by an open fire from beneath must have been very imperfect, and the evolution of chlorine but slow. As there was no grating, much manganese must have been lost, especially as, in the absence of an agitator, ground manganese could not be used to advantage, though it seems to have been used. A still patented by Boyd (June 2nd, 1853), made of

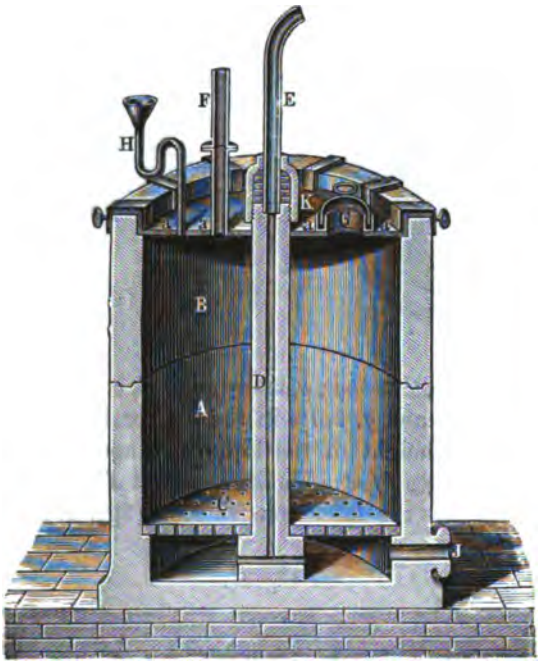
Fig. 43.




cast iron with a firebrick lining, set in mortar of pipeclay, ground pitch, sand, and boiled oil, is quite unworkable.

A much better chlorine-still is represented in fig. 44. The apparatus, made of scooped-out blocks of sandstone, is about 6 feet 6 inches high and 3 feet 3 inches wide, hence made in two pieces (A and B), which are rebated together in the middle and joined with clay and boiled oil. A also includes the bottom; the thickness of the sides up to 6 inches above this is a little more than higher up, so that a recess of 2 inches all round is formed, on which rests the perforated plate C, on which the manganese (in pieces) is placed. D is the steam-pipe made of sandstone, connected by E with the main pipe; the steam can only escape below the false bottom, by the perforations of which it is well distributed. The top of this still was made of lead (stone would be much better), and was provided with openings for the chlorine-pipe F, the man-hole G, the acid-funnel H, and the steam-pipe E. The lower opening, J, closed by a wood plug, serves for discharging.

Fig. 44.




A peculiar form of still was patented by Lee on August 4, 1841, viz. shallow stone troughs covered by shallow brick arches, in the shape of an oven. They stood on an open foundation beneath, and were heated from the top through the arch by an open fire. In order to make the tops gas-tight, they were covered with a mixture of fireclay, ground fire-brick, and common salt. Evidently in these ground manganese was employed; and cracking the bottom was avoided by not heating it. But in this way these stills must have been very imperfectly heated; and they were soon given up again, as appears from the fact that Mr. Lee's partner, W. W. Pattinson, on July 14, 1846, patented a new form of still, an improvement of which was the subject of a fresh patent on April 6, 1852, and was in use at the Felling works near Gateshead up to the time of the introduction of the Weldon process. This apparatus already exhibits all the parts of modern stills, and was moreover specially protected against cracking and against dilution by condensed steam.

Figs. 45 and 46 show its first construction. *a a* is a circular

Fig. 45.

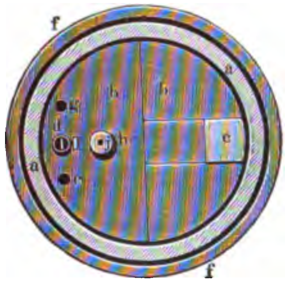
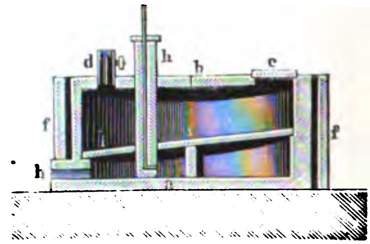


Fig. 46.



still, made of stone, *b* its top; *c*, man-hole; *d*, chlorine-pipe; *i*, false bottom (grate); *e* and *g*, holes in the top for introducing the acid and gauging the height of the liquor; *h*, aperture admitting the stone steam-pipe *j*; *ff*, double iron jacket for heating the still from without. In the later construction (figs. 47, 48) the inner

Fig. 47.

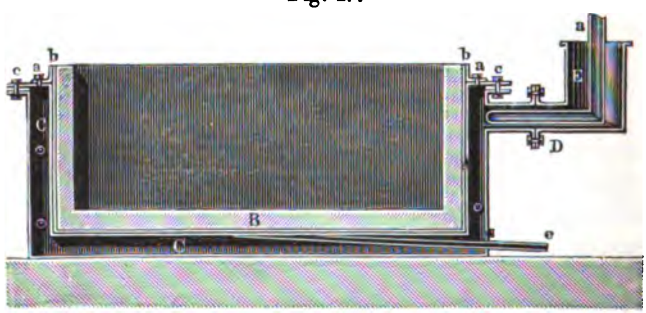
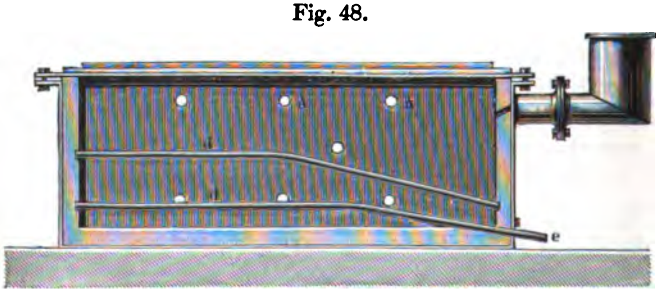


Fig. 48.

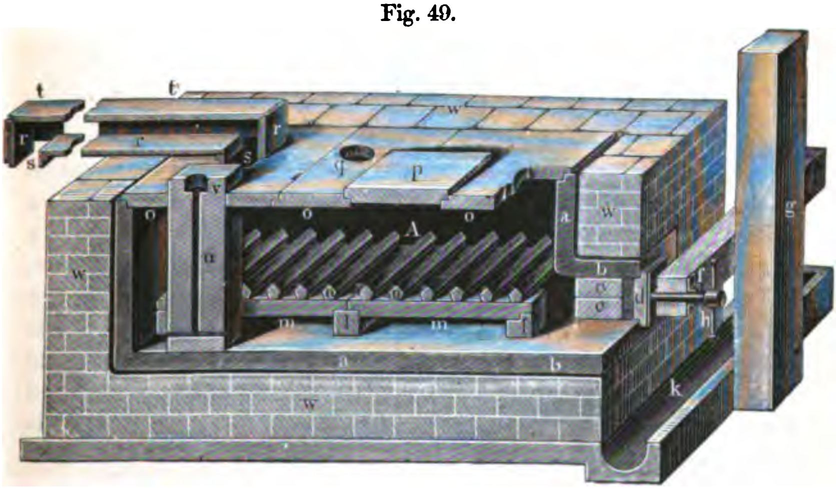


iron jacket A is perforated by a number of holes; the stone vessel B is 6 inches higher, and its projecting portion is surrounded by the iron ring *a a* which leaves a small caulking-space *b*, and has a flange which is bolted to the flanges of the iron jackets A. The joint is made by indiarubber washers and melted lead. The small iron reservoir E communicates through D with the space between the stone and the iron jacket, and with the annular space C between the two jackets; the steam-pipe, *d*, coils several times round the stone still and comes out at *e* (fig. 48, which represents the jacket without the still). Into the vessel E hot coal-tar, boiled down to the consistency of pitch, is poured till the whole space C C is filled; and this is always kept hot by the steam-pipes; so that the still is heated from without, and at the same time its cracking prevented by the uniformity of heating. Even if the stone should still get cracked, the work may be continued, since the tar prevents the acid from getting out. This construction is somewhat expensive, especially from the necessity of making the inner vessel from a single block of stone; and therefore its use has not been very widely extended.

Lister's patent (Jan. 11, 1854) leaves spiral channels within the sides of the still itself, for heating it by means of steam or hot air —an unpractical construction.

At several German works there are found chlorine-stills of the shape represented in fig. 49. A is a square box, consisting of the

Fig. 49.



proper still *a a* and the brick jacket *w*. The still *a a* is cut out of a single block of sandstone, and covered with a slab of the same material; where such large blocks cannot be had, the stills are composed of several pieces. In any case the sandstone is boiled in tar till it absorbs no more of it. The sides are 6 to 8 inches thick, 6 ft. 6 in. long, 3 ft. 6 in. wide, and 2 ft. 6 in. high. The brick jacket is 10 inches thick, and leaves between itself and the still an inch space, which is filled with melted pitch. A little above the bottom a grate *n n*, consisting of sandstone, lies on the sleepers *l l* and *m m*; upon this the manganese-ore (about 10 cwt.) is charged through the man-hole; the lid of the latter is made tight with red lead, pipeclay, and boiled oil. The acid arrives through the pipe *q*, the steam through the sandstone column *u v*. A sandstone flue, *r s t*, conveys the chlorine gas to a second still and then to the chambers. The wide neck *b b* serves for discharging the residues into the shoot *k*; it is closed by bricks coated with moist clay, upon which the sandstone lid is placed and made tight with clay. By means of the wooden post *g*, the movable crossrail *f*, and the screwbolt *h*, the lid *d* is pressed tightly against the still; it is protected from fracture by an iron plate. The acid is run in by a lead box and siphon, fig. 50, the longer limb of which is cemented into

Fig. 50.


the hole *q*. When the acid has risen to the dotted line *a* the siphon begins to run, and empties the whole vessel, which usually holds a carboy full of acid. [This is a very clumsy contrivance; why should the acid first be filled into fragile carboys and one such run in at once, instead of running it in directly from a tank and regulating its flow by an earthenware cock? The grating *n n* is also very unsuitable, especially liable to break; so is the gas-flue *r s t*, which is in every way inferior to good stoneware pipes; and there is no opening for gauging the height of the acid, which has to be done through the man-hole!]

The stills mostly employed in England for the last 20 years, which even since the introduction of Weldon's process are still required for decomposing the fresh manganese, are shown in figs. 51 to 54; but of course there are differences in detail. The corners, especially in Lancashire, are often, and on the Tyne always, made in a somewhat different way, viz. with feather-and-groove joint, as shown in the case of condensers in figs. 105 to 108 (Vol. II. pp. 199, 200). Fig. 51 shows a still seen from above; fig. 52, in front; fig. 53 a section through A B, and fig. 54 a section through C D, of the plan, fig. 51.

Fig. 51

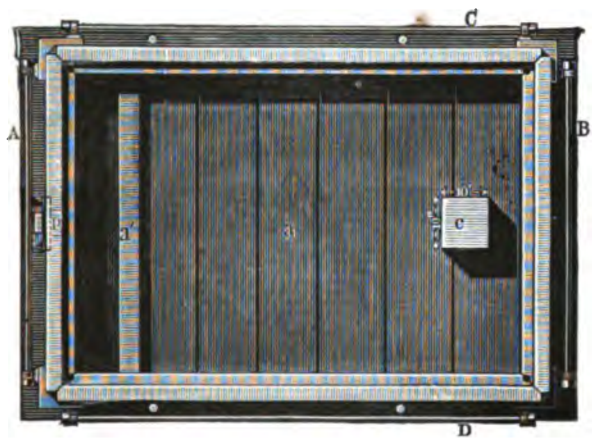



Fig. 52.

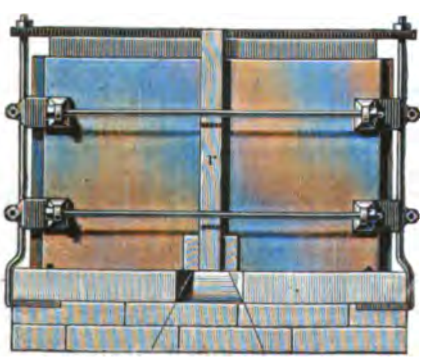


Fig. 53.

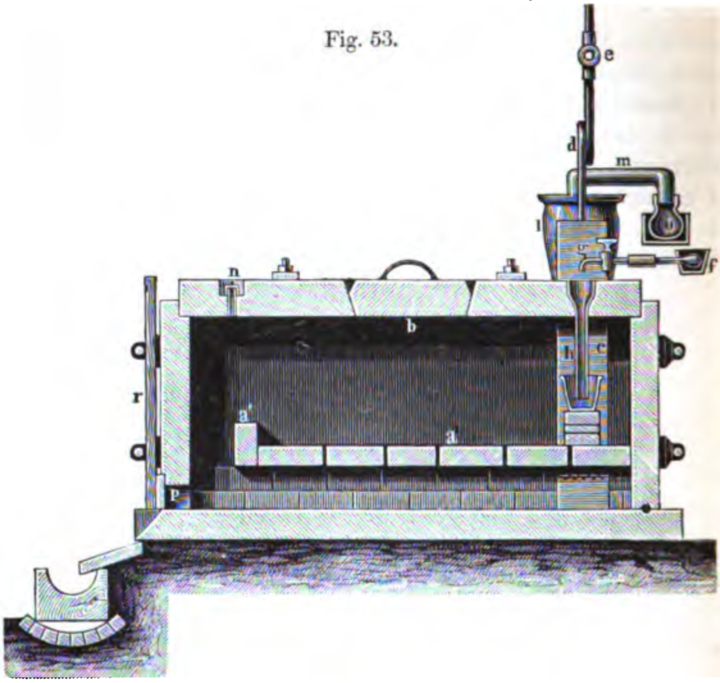



Fig. 54.

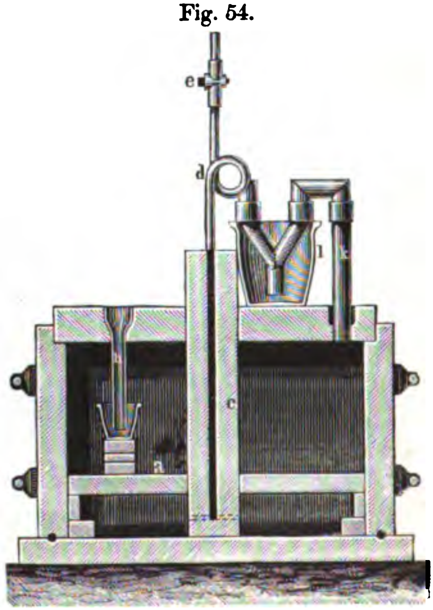


Fig. 55.

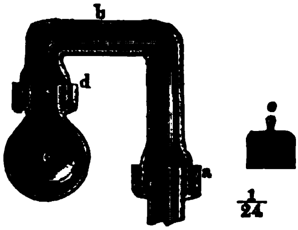



Fig. 56.

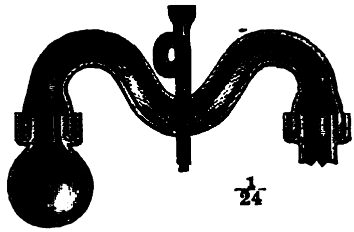
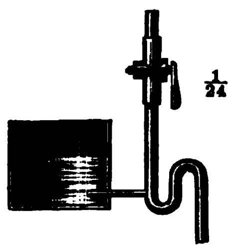



Fig. 57.




The stills are built of flags of siliceous sandstone from Halifax, in Yorkshire, Felling-on-Tyne, &c. If the stone is at all porous, it is first boiled in tar; or the still, after being put together, is filled with tar, and this is boiled for some time by means of steam. Stills made out of a single block are occasionally used, but always of smaller dimensions than those drawn. In the construction as shown in the diagrams the joints of the side flags with each other and with the bottom flag are made tight by indiarubber cord about $\frac{3}{8}$ inch thick; when feather-and-groove joints are employed, the well-known tar-and-fireclay cement is used. The manner of binding together the flags by iron ties can be seen from the figure; this, as well as all other details of construction, has been exactly described in the case of acid-tanks (Vol. II. *l. c.*). The stills must have a very substantial foundation, lest they should settle down from their weight, which always causes leakages. The foundation cannot be set with lime-mortar, but only with tar and sand. The bottom stone is 9 to 12 inches, the sides and top are 6 to 8 inches thick; the top may consist of two pieces. The parts peculiar to chlorine-stills are as follows:—First a sandstone grate *a*, consisting of sleepers placed close together, as their rough sides do not touch closely enough to prevent the acid getting through; this permits

employing manganese even in the state of fine powder. Sometimes the front sleeper *a'* is placed upright as drawn, in order to facilitate the circulation of the acid; but then care must be taken on charging the manganese through the man-hole, lest any of it fall over the sleeper *a'*. The grate is pierced so as to allow the passage of the square stone or stoneware pipe *c*, of 1 inch bore, which below the grate has three side openings; it is joined on the top, by cement, to the lead pipe *d*, which beyond the cock *e* is continued into an iron steam-pipe, branching off from the main pipe. The loop of the lead pipe *d*, after the steam is shut off, at once fills with condensed water, as the cock *e* is never quite tight, and thus preserves the latter for some time from corrosion by the chlorine gas, which rises up in the steam-pipes when the steam is shut off. On starting the steam again, the water is blown into the still. But it takes a little time for enough condensed water to collect to protect the cock against chlorine; and in the meantime the cock is strongly acted upon. A complete cure for this is afforded by the contrivance shown in fig. 57. Here the bend of the steam-pipe is connected by a small leaden branch pipe with a lead box of 12 inches square and height, in which water stands almost up to the level of the bend of the steam-pipe. The branch pipe is closed at the end, up to a pin-hole, through which in the state of rest the bend is filled with water. On starting the steam it blows the water into the still; a little also blows through the pin-hole into the water of the lead box, condenses there, and replaces that blown away before. When the steam-cock is shut, the water instantly runs through the pin-hole back into the bend, and protects the cock above from the chlorine gas below. In this way the cocks last five or six times as long as with the ordinary arrangement. The muriatic acid runs from the main pipe *f*, through the branch and cock *g*, into the earthenware pipe *h*, which stands in a pot, so that an acid lute is formed and no chlorine gas can get out. The opening *n*, closed by a hydraulic lute, serves for gauging the height of the acid. The chlorine gas escapes through the 3-inch earthenware pipe *k*, the connexion and disconnexion of which with the main gas-pipe *o* is here effected by a very simple apparatus. The pipe *k* is continued into a Y-shaped pipe *i*, open at the bottom and standing in a large earthenware pot *l*; the other limb of *i* is connected by the bow *m* with the main pipe *o*. When water is poured into the pot *l* above the level of the point of junction of the two limbs of *i* (as in fig. 54), the still is cut off

from the gas-main, and can be cleaned and charged; but if the water is partly run out of *l* by a siphon or cock, the gas can pass through and the still communicates with the gas-main. The lower end of *i* must always be luted by water. In the place of this very simple and efficient contrivance many others are employed, often causing a loss of gas in handling them. One of the simplest and most frequent is shown in fig. 55. To each branch pipe *a* there corresponds, on the main pipe *c*, a water lute, formed by two concentric rings of 4 or 6 inches depth; and a similar water-lute is also made on *a* itself. If the still is to be connected with the gas-main, the bow *b* is put on; if it is to be cut off, the bow is taken out and the cap *e* put on. But during this change gas always comes out of the main pipe. Another simple cut-off, which is not subject to this drawback, is shown in fig. 56. If the still is to be cut off, water is poured through the funnel into the bent-down portion of the connecting pipe between the still and the gas-main, till the connexion is interrupted; if it is to be made again, the water is removed from the pipe by pulling out the bottom plug. Figs. 51 and 53 also show the discharging-hole *p* for the manganese-liquor, which is always mixed with much mud. Ordinary cocks or valves are not applicable here, for reasons easily understood. The discharging-hole has the shape of a D lying on its side, and goes down to the bottom, which is sometimes inclined towards it; it is closed by a plug of wood wrapped round with brown paper and driven in with a hammer; but in the drawing another kind of fastening is indicated, viz. a lath *r* reaching down between the tie-rods and the stone, which squeezes the plug against the hole *p*. These running-off holes are a great nuisance; they might be closed much more safely, *e. g.* in the way shown in fig. 49, or still more so in that to be described for Weldon's stills; but that is not quite so easy here, because they have to be very frequently opened (every 24 or 48 hours). But it might be arranged to employ a large stoneware cock, say 3-inch bore, as in the Weldon stills, for daily use, and a man-hole only to be opened now and then. Sometimes the pressure within the still forces out the plug and with it all the contents of the still. In order to catch the liquor violently shooting out in this case, and also in the ordinary discharging, the stills are placed in two rows, between which runs a gutter for the liquor; in front of the stills a pavement is made of tightly-joined flags, with considerable descent to a gutter in the middle. The latter is

either made of long hollowed-out stones, or, as it is very difficult to keep the joints tight against the hot acid liquor, it consists of a single large balk scooped out in the shape of a gutter. If several such balks are to be connected lengthways (and the same holds good of the joints of stone gutters), the joints are half-lapped and made as tight as possible with hard pitch &c. The balks are made of American pitch-pine, 2 feet thick and 50 to 60 feet long, with a 12-inch gutter scooped out; they are laid with sufficient fall to convey the liquor quickly into the mud-well, where the clear liquor is separated from the mud. In order to be quite safe against any leakage through the gutters, which unavoidably causes settlings and leakages of the stills, and may even damage the stability of the building, sometimes an inverted arch of firebricks set in tar and fireclay is made underneath the gutters. All this is saved when the stills only serve for working the manganese destined for replacing the unavoidable loss in the Weldon process; for then they are placed at a suitable height to run their contents straight into the Weldon still by means of a 3-inch stoneware pipe and cock.

Exceptionally, stills are provided with a jacket of stone or brickwork, in order to heat them by steam from without and save some of the steaming within. The latter cannot be avoided entirely, because the heating through the 6 inches of stone is never sufficient; but the outside heating goes some way, and prevents to some extent the dilution of acid by condensed steam; but, on the other hand, cracks and leaks of the inner still are only perceived when they have gone very far and are difficult to repair. This also holds good of a brick jacket with a layer of puddled clay between it and the still for the purpose of preventing the radiation of heat and making any leakages harmless. They really do not do this; for the jacket itself, whenever the acid gets to it, is soon perforated, and then only prevents the discovery of the leak.

All parts of the still, wood, iron, lead, or stone, are well painted with coal-tar, and this paint is frequently renewed; otherwise they are soon wasted away, more especially the ironwork.

On laying out a factory, attention must be paid to giving fall to the hydrochloric acid from the condensers, or from the acid-tanks, to the main pipe *f* and thence to each still. The acid-pipes are made of stoneware, joined by sockets and cemented with tar and china-clay or boiled oil and pipeclay. Very suitable, indeed, is the arrangement described in Vol. II. p. 259, consisting of an india-

rubber ring round the pipe within the socket, in lieu of cement. The pumping of muriatic acid is avoided whenever possible; the contrivances serving for this purpose are described in Vol. II. p. 255 *et seq.* Only at very small works is it possible to collect the acid in carboys and charge it by hand into the stills.

*Stills made of stoneware* were formerly very generally employed, and are so even now in bleach-works and paper-mills bleaching by gas; in France they are found even at very large works, *e. g.* at Chauny. If they are to be at all serviceable, the greatest care must be taken in selecting the clay and manufacturing them, even more so than for hydrochloric-acid receivers; and the remarks made in Vol. II. p. 205 hold good even more absolutely in this case. They are made of various shapes. That shown in fig. 58 is intended for manganese in lumps, which is charged after lifting off the top *a a*, resting in a water lute; *b* is the acid-funnel, *c* the water lute for the gas-pipe. The shape most usual in France and partly in Germany is shown in figs. 59 and 60. The two smaller necks serve for introducing the acid and taking away the gas; the large central opening serves for suspending the stoneware sieve, which is covered by the lid *b*. The holes in its lower part are of about $\frac{3}{8}$ inch diameter; in the upper part there are two larger holes for lifting out the whole sieve by means of specially shaped tongs. The sieve is filled with about 1 cwt. of manganese in small pieces; mostly the acid has already been poured into the jar; and the sieve is now suspended and the lid put on immediately and made tight by clay, boiled oil, and Stockholm tar. These jars are always heated from without, four or eight of them being placed in a wooden box lined with lead, or a box made of bricks set in cement; this acts as a water-bath, heated by steam; or it is filled with a calcium-chloride solution and heated by a steam-coil; or the box is left empty and the steam heats the jars directly. At the end of the operation the still-liquor is drawn off by a siphon, or by a discharge-pipe passing through the steam-jacket. These small stills in proportion to their turn-out require much manual labour; but they are cheaper than stone stills, and give a very good yield of chlorine from the acid, as this is not at all diluted by steam. In these stills only 6 to 10 per cent. of the acid is lost in the still-liquor, against 30 to 50 per cent. in stone stills; hence where hydrochloric acid is valuable, the stoneware stills pay better, in spite of the increased labour. In the south of France they have

Fig. 58.


Fig. 59.

Fig. 60.

recently replaced the former stone stills (Balard, 'Rapport du Jury International,' 1868, vii. p. 48); but there are also examples of the contrary, especially in Germany.

The *work* that goes on with the large stone stills is as follows:—The still, properly cleaned from the previous operation by lifting off the grates and rinsing it out with water, is put right again by stopping up the discharge-holes, and putting in the grate-sleepers. It is then charged with the requisite quantity of manganese; say 6 to 10 cwt., according to its size. The manganese ought to be in pieces not exceeding the size of a hen's egg, and less. The man-hole lid is put on, and the joint made good with wet clay. This, unless it is always kept moist, cracks and allows gas to escape; it must consequently be watered from time to time, as well as all other clay joints and water lutes; and for this purpose no still-house ought to be without a water-pipe and hose long enough to reach every still. A better cement, but dearer, is made of pipeclay and boiled oil, which is generally used only for permanent joints. Tar and fireclay is not very suitable for this purpose, as it becomes too hard. Then hydrochloric acid is run in till the still is three quarters full, which is tested by a gauge-rod through the hole provided for this purpose. At first the acid is run in quickly, but afterwards, when more chlorine is being evolved, more slowly; so that it takes several hours before the still has got its charge of acid. The evolution of chlorine begins at once, without applying any heat, and the more briskly the more concentrated the acid is. The concentration should be as high as possible; for as the loss of HCl in still-liquors is to a great extent connected with their bulk, a certain bulk of still-liquor always containing about an equal quantity of free acid, much less acid is lost if it was originally concentrated than if it was weak. This proportion becomes still more unfavourable for weak acid from the fact that with the latter more steam must be blown in, which again dilutes the liquor with condensed water. The lowest strength of acid allowable for chlorine-making is 18° Tw.; but at this strength about 50 per cent. of the acid is found in the still-liquor, whilst factories working with acid of 30–34° Tw. only lose from 25 to 30 per cent., and still less with indirect heating. It is true that this loss is not of any great importance when the still-liquor is first passed through a Weldon still, where its free acid is utilized in the end; to a certain extent this is also the case with some systems of sulphur-recovery from tank-waste.

The evolution of chlorine continues for some time, say 8 or 12 hours, without any heat being applied; but after that, to supply the necessary heat, steam is usually blown in. This is done at intervals, seldom continuously, because the temperature would be apt to rise too much. On the Tyne it is a common rule to steam for ten minutes every hour. Care is required lest by too violent an evolution of gas the water be thrown out of the lutes and the gas escape from all the joints of the stills, pipes, and chambers. Hence the stills should not all be steamed at the same time, but alternately—*e. g.*, in a set of 12 stills, two at a time for 10 minutes, so that the turn of the first two comes round again an hour after. Steaming in excess moreover causes much water and HCl to get into the gas-main, and, in spite of collectors, also into the chambers; and thus a single mistake of this kind may spoil a whole chamberful of bleach, or at least prevent it from getting up to full strength. At the same time such neglect creates an intolerable nuisance to the whole neighbourhood, and that in a far higher degree than any escape of hydrochloric, nitrous, or sulphurous acid.

By the successive steamings the temperature of the contents of the still gradually increases; but it ought never to exceed 90° C., because otherwise too much water and HCl escape. When the gas has been driven off as much as possible, the steaming is stopped, the bottom plug is knocked out, and the still then empties itself in a few minutes. This is done once in 24, 36, or 48 hours; the longer the contents of a still can be kept in, *i. e.* the more still-room is provided, the more chlorine will be got from a certain quantity of acid, and the less free chlorine will be present in the still-liquor. Still there is always enough chlorine present to produce a fearfully suffocating stench on discharging the hot still-liquor. Hence in many works this operation is performed between three and four o'clock in the morning, when there is least life stirring in the streets and houses—certainly a very unsatisfactory evasion of the difficulty. Some other plans have been tried—*e. g.* covering with boards the gutter and the mud-well into which the liquor first runs, and drawing off the gas into a brick tower fed with milk of lime. This is a considerable step forwards, but not quite sufficient. There still remains the enormous contamination of all sewers, watercourses, &c. into which the still-liquor runs. All this is avoided in the Weldon process, where by suitably placing the stills the acid still-

liquor is run immediately into the large mud-stills and does not come into contact with the atmosphere.

Frequently the manganese is not all decomposed in one operation; in this case, after opening the man-hole, about half the usual charge of manganese is put in, and the still cleaned out only after the second operation. This is especially necessary with the harder descriptions of ore.

In the chlorine-stills the first reaction is

$$2MnO_2 + 8HCl = Mn_2Cl_6 + 4H_2O + Cl_2.$$

(The high probability of this is demonstrated by Pickering, Journ. Chem. Soc. Sept. 1879, p. 654, who maintains the non-existence of the compound $MnCl_4$, the formation of which is asserted by W. W. Fisher, ib. Sept. 1878, p. 409.) The sesquichloride, $Mn_2Cl_6$, which yields a dark brown solution, is not stable even at the ordinary temperature, and quickly decomposes into $2MnCl_2 + 2Cl$; but this decomposition is only completed at a little below 100° C. Accordingly, for 100 parts of pure $MnO_2$ or an equivalent quantity of manganese-ore, almost exactly 170 dry HCl or about 530 acid of 32° Tw. ought to be consumed; actually at least 10 per cent., frequently 100 per cent. more are used, for the reason above given:—*i. e.* the maximum with hard and low-strength manganese, weak acid, and direct steaming; the minimum under the reverse conditions.

Sometimes the chlorine gas is *dried* by conducting it through a coke-tower fed with strong sulphuric acid. This is done especially when it has been first washed with water in order to deprive it of hydrochloric acid and of any iron and manganese salts carried away with it. This plan is rarely followed except in connexion with the Deacon process, where the large quantity of acid left undecomposed makes it unavoidable—or for special purposes, such as the manufacture of anhydrous stannic tetrachloride; but if some cheap plan could be discovered for drying the chlorine gas completely, it would be far easier to get up the bleach to the highest strength, because this depends upon exactly regulating the moisture present (comp. pp. 108 and 157).

The *pipes* for conducting chlorine gas are usually made of lead, but may just as well be stoneware if they are joined by a permanently somewhat soft and elastic cement; in this respect oil-cements are better than tar and fireclay. The pipes ought to be long enough to cool the gas, and to condense any steam and HCl carried along,

before the gas gets into the bleach-chambers. They are made to descend towards a collector of stoneware or lead placed near the chambers, from which the condensed acid water runs off, either from time to time or continuously, through a swan-neck pipe. Sometimes these collectors are filled with manganese-ore (but never with limestone!). In colder climes the pipes ought to be protected by a light roof from being cooled down too much in winter; otherwise they may become plugged up by the formation of chlorine hydrate (p. 84). Leaden pipes must be so laid that they may expand and contract with the changes of temperature.

Weldon (patent, Nov. 4, 1871) proposes purifying the chlorine gas by a mixture of magnesium chloride and quicklime, or by common salt. Hargreaves (pat. Nov. 25, 1871) proposes to deprive it of HCl by lime, magnesia, or manganese-ore (this is nothing new), or to make an impure bleaching-powder and obtain pure chlorine by decomposing that. Neither of these processes seems adapted for the ordinary manufacture of chlorine, but only for that obtained in a dilute state and containing much acid.

# CHAPTER III.

## THE MANUFACTURE OF BLEACHING-POWDER.

The lime intended for manufacturing bleach must be of special purity; on this depends to a great extent the possibility of making strong and durable bleaching-powder. This means, first, that the limestone should be sufficiently pure, and that it should be burnt as well as possible. Most manufacturers, in order to make sure of the last point, prefer burning the lime for themselves. The Lancashire manufacturers enjoy the advantage of getting, delivered by rail to their works, an extremely pure and well burnt limestone from Buxton, which has the agreeable property that, on shaking it, all the unburnt portions remain behind as stony pieces (yelks), so that the fine powder of calcium hydrate is almost completely free from carbonate. Most descriptions of lime do not behave in this way; and the bleach-manufacturers can ensure their sufficient freedom from carbonic acid only by taking the burning in hand themselves.

Limestone, to be employed for bleach, must contain very few constituents insoluble in acid (clay, sand, etc.), because otherwise (as of course they would not be converted into bleach) the strongest article could not be made. Moreover bleach containing clay settles imperfectly and very slowly on being dissolved, and is on this account disliked by bleachers, paper-makers, etc. Consumers also require a white article, which excludes iron, manganese, etc. These metals are even said to impair the durability of bleach; but this is not certain. Magnesia is also very much disliked, because, it is said, the deliquescence of magnesium chloride interferes with the stability of bleach. This does not appear to have been certainly

proved; but, for instance, the magnesian limestones found on the Tyne, from the coal-measures and the Permian, have been found quite unsuitable for bleach-making. On the other hand, a dark colour of the limestone, caused by bituminous matters, is quite harmless, as these are destroyed by the burning. Balard (Rapport du Jury, vii. p. 49) asserts that the physical are even more important than the chemical properties of limestone in regard to its suitability for bleach-making; according to him, pure but crystalline limestone is not suitable, while another description, containing more than 2 per cent. sand and clay, is preferred at Chauny. This assertion is contradicted by experience. The author has never made finer and stronger (39 to 40 per cent.) bleach than with a cargo of distinctly crystalline limestone from the north of Ireland which he got by chance. At Chauny (cited by Balard), at any rate at that time, as a rule the bleach made contained not 35, but only 30 to 32 per cent.

It cannot, however, be denied that the physical properties of the limestone, or rather of the lime made from it, have a good deal to do with the quality of the bleach. "Fat" lime, which slakes quickly and yields a fine, light powder, absorbs chlorine much more quickly than poor lime which on slaking yields a gritty powder, even when analysis does not show any difference between them. Bleach from fat lime also keeps much better than that from poor lime. The latter contains much more chlorate, and is more ready to decompose with evolution of gas; but the former more easily attracts moisture from the air and becomes pasty (Wright, Chem. News, xvi. p. 126).

On the Tyne the usual material for bleach-making is a hard chalk closely resembling limestone, from the lower reaches of the Seine, whence it is brought by colliers as ballast, and is known as "French cliff." It is very pure calcium carbonate, contains next to no iron, and only fractions of 1 per cent. of constituents insoluble in hydrochloric acid. It is also tested by scraping with a knife, when it should yield a floury, not a gritty powder. The bleach made from it is much more bulky than that from Buxton or Irish limestone; so that about ⅕ more casks are required for it. The solutions of bleach made from cliff do not settle so quickly as those of limestone bleach; bleachers usually prefer the latter, papermakers the former.

The *burning* of the limestone may take place in any lime-kiln, so

long as the lime cannot be contaminated by the ashes of the fuel, or as the more impure portions are kept out and used for mortar

Fig. 61.

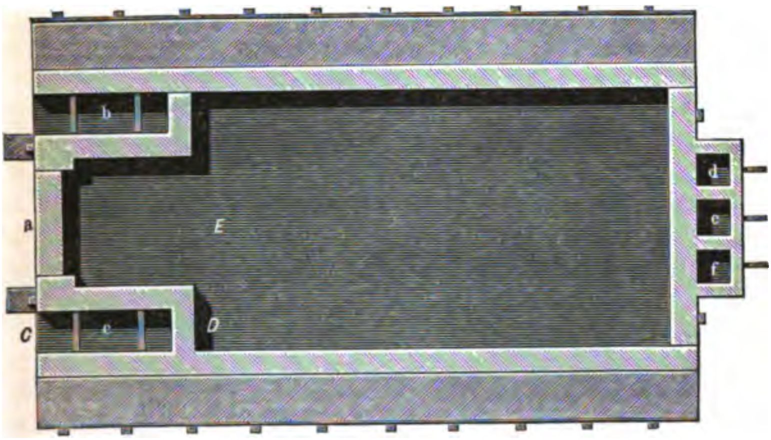
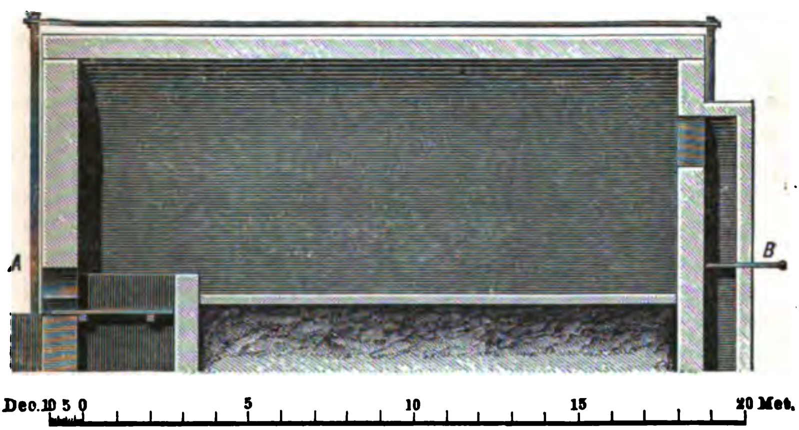



Fig. 62.




etc. The most rational are the circular or other continuous furnaces, which are now also in use at Buxton. But a bleach-manufacturer cannot possibly manage with furnaces turning out such large quantities; he must therefore build kilns of another kind.

Those employed on the Tyne are of the shape of a horizontal reverberatory furnace, as shown in figs. 61–64. Fig. 61 is a plan on the line AB of the sectional elevation, fig. 62; the latter is taken on the line CDEF of the plan. Fig. 63 is a front elevation, fig. 64

Fig. 63.

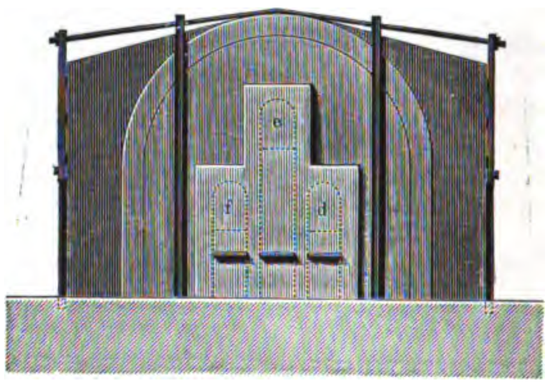
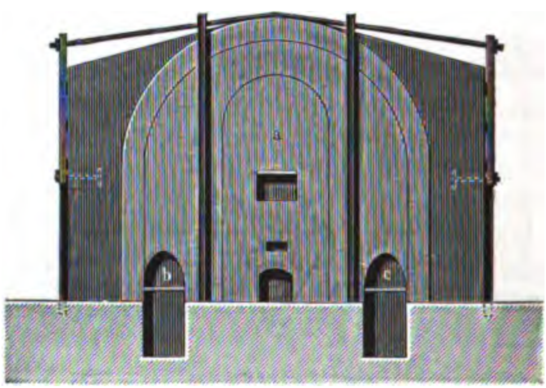



Fig. 64.




a back elevation. In front there is a larged overarched opening, *a*, for charging and discharging the kiln; after putting in the limestone, it is closed by a temporary wall, in which the three stoke- and peep-holes seen in fig. 64 are left. Besides, there are the

small fireplaces *b* and *c* with grates: sometimes the latter are wanting, and the coals are heaped up behind the stoke-hole; but that is not a good arrangement. In the semicircular arch which forms the kiln-roof, one or two circular holes, 14 inches wide, are made, but covered up during the burning; they serve for more quickly cooling and airing the kiln. Both the arch and the lining of the kiln all over consist of the best fire-bricks; and the kiln is well braced with uprights and tie-rods. Three snore-holes *d, e, f*, each of them connected with a small shaft and damper, carry away the products of combustion; only below ground the three shafts combine to form a main flue leading to a good chimney. In this way the draught can be regulated equally all over the kiln.

This kiln is intended for bituminous coal. For sandy coal or brown coal a gas-generator is to be preferred, as indicated (in figs. 229–233, Vol. II. pp. 527–537) for a calcining-furnace, unless the horizontal kiln be replaced by an upright one.

The limestone is put in thus:—From the largest lumps (12 to 15 inches wide) three flues are made, corresponding to the stoke-holes and snore-holes; they are covered up with larger blocks, these with smaller lumps, and the smallest (down to the size of a fist) on the top, the kiln being filled right up to the roof. Of course the commencement is made at the back end, and a section of an arm's length finished right up to the roof before the next one is begun. At last the door is walled up as drawn, leaving the draught- and stoke-holes, which are closed with loose iron plates. The firing is now begun from all three stoke-holes, and is continued till the whole contents of the kiln have been burnt to quicklime, but not burnt "dead." This point is reached when a look through the peep-hole shows that the kiln is white-hot up to the roof, and that the charge has sufficiently settled down, owing to the diminution of volume of the limestone in being converted into quicklime. The exact amount of this cannot be stated, as it depends upon the size and shape of the kiln and the nature of the limestone. Although regard for economy of fuel might seem to point to making the kiln very long, this is not feasible, because the bad portions would be burnt too late, and the first portions would consequently be already burnt dead. The dimensions as drawn are proved to be right by experience. The lime is well burnt when it contains less than 2 per cent. $CO_2$; if the latter exceeds 3 per cent., the lime should be rejected altogether for bleach-making.

A kiln of the size represented holds about 10 tons of limestone, and requires about 5 tons of coals for a burning. With good coals and careful teasing, the burning last four days and nights, sometimes five. At the end all the openings are plastered up, also the dampers; lest the kiln should crack by cooling too quickly; after 24 hours the dampers, ash-pits, and top holes are opened, then also the temporary front wall; and as soon as the kiln has cooled down so that it can be entered, the lime is taken out. If, however, for any reason the lime is not required at once, but is to be kept for some time, the openings are left plastered up as well as possible: the quicklime is then found perfectly good even after months.

Interesting experiments on the temperatures at which, on the one hand, CaO absorbs $CO_2$, and, on the other hand, $CaCO_3$ is dissociated, have been made by Birnbaum and Mahn (Ber. deut. chem. Ges. xii. p. 1547).

*Slaking* the quicklime is very simple work. The lime is spread on a brick floor (protected from rain) to a thickness of 12 or 15 inches, and water sprinkled over it by a watering-pot or a rose attached to a water-hose, till the formation of calcium hydrate is indicated by the well-known appearance of heating, emission of steam, and swelling-up of the lime. Every portion of the lime must be turned over with a spade, in order to promote its slaking, and a little water added from time to time, till at last every thing that can be slaked at all has fallen to a light fine powder. The workmen protect their mouths and noses during this operation, and during the sifting of the lime and charging of the chambers, by "muzzles" such as will be described hereafter. The large unslaked pieces are picked out and thrown away, if they are pebbles or flints; and any pieces of unburnt limestone or lime burnt dead can be ground and employed in the soda-mixture or for neutralizing the manganese-liquors in the Weldon process; but they may not after grinding be mixed with the sifted calcium hydrate, as stated here and there.

The calcium hydrate must in any case be *sifted* through brass or iron wire-gauze or hair sieves. At some works sieves with 12 holes, at others sieves with 25 holes to the linear inch are used. It is found that the finer the lime is sifted the better it absorbs the chlorine. The sieves, cylindrical or hexagonal, lying in a closed box in an inclined position, the hydrate is put in at the higher end; and at the other end only the coarse particles are brought out by

the sieves, all the fine dust now being found in the box. The coarse parts (lime riddlings) are employed for mortar etc. At larger works the turning of the sieve is done by a small steam-engine, which also drives a revolving brush inside it; thus the powder is pressed against the wires, and there is much less waste in the shape of "riddlings."

The sifted lime is either kept in large wooden boxes or in small casks, arranged for easy carriage to the chambers (old petroleum-casks). It has been found that lime freshly slaked is not so suitable for bleach-making as when it has been lying for a few days. This long-known fact has been sometimes attributed to some mysterious change, or even to the absorption of a little carbonic acid and moisture from the air—which is quite erroneous; such absorption, should, on the contrary, be prevented. The true cause is simply that the lime requires some little time to be slaked completely through, and to cool down entirely—the latter being a slow process, owing to the loose, porous state of calcium hydrate and its being a bad conductor of heat. If some manufacturers, as is stated, avoid the action of sunshine on the lime, this must be for the same reason, viz. because the heat of the sun retards the cooling.

It is a perfectly established fact that the lime from which bleach is to be made should not be dry $Ca(OH)_2$, but should contain some water in excess, although it has been proved, contrary to previous assertions, that even perfectly dry calcium hydrate absorbs chlorine (see pp. 102 & 108). But opinions differ very much as to the proper quantity of water in excess, viz. from 2 to 15 per cent. Frequently it is assumed that there ought to be from 6 up to at most 8 per cent. of water along with $Ca(OH)_2$; but from very careful experiments, made by Schäppi in the author's laboratory, it would appear that with chlorine of the ordinary degree of moisture the strongest bleach is obtained, if the lime approaches as nearly as possible to the composition of real calcium hydrate—*i. e.* 24·5 per cent. of water. At the Aussig works the lime is put into the chambers with 24·5–25 per cent. of water in summer, and with 25·5 per cent. in winter, because then the chlorine is deprived of more moisture in its 200 feet passage through the gas-pipes. Thus the bleach is obtained daily of uniform strength with the greatest regularity. A larger proportion of water favours the absorption of chlorine; but then close lumps are formed which enclose much undecomposed lime. There are lumps found even in perfectly good and strong bleach; but these are dry, easily broken, and porous,

and changed into bleach right to the core; they cannot be confounded with the damp lumps formed by damp lime and especially by moist chlorine. Under no circumstances should any particles of unslaked lime get into the bleach-chambers.

*The Bleaching-powder Chambers.*

The action of the chlorine (evolved by any sort of process) upon the lime takes place, of course, in very different apparatus, according to whether dry or liquid bleach is to be made—that is, whether calcium hydrate or milk of lime is employed. We shall first treat of the former and much more important kind.

The lime is treated in the so-called bleaching-powder chambers or "boxes," each of which consists of a closed space built of a material resisting the action of chlorine gas, but which widely differ as to their sizes, their inner arrangements, and the material they are formed of. During the first period the chambers were made of wood, very tightly joined together in double layers, and coated with a thick paint of asphalt. Such wooden chambers cannot be kept tight if the pressure of gas gets beyond a very moderate amount, and hence are useless for strong bleach. Other chambers (now very much more rarely found than formerly) are made of tarred sandstone flags or slates, the flags being joined together by rabbets and tar and fireclay. These chambers are gas-tight enough, if properly built and standing on a substantial foundation (which prevents settling); but they are unsuited for large works, because they are very costly, and can only be made of a moderate size, which also involves much labour. They can be made larger, if the top is not made of stone flags, but of tarred wood; but this plan again waives the advantage of a substantial erection. In order to better utilize the expensive stone chambers, they are mostly provided with stone shelves (sometimes, but very wrongly, with wooden shelves, from which splinters get into the bleach), so that a larger quantity of lime can be got into them. This kind of erection existed at many English works 10 or 15 years ago; but it has been given up almost entirely, since it has been found that even in a chamber 6 feet high the lime at the bottom absorbs the whole of the chlorine; the latter, being much heavier than air, always tends to sink down when the layers below have become poorer in chlorine by absorption. The shelves thus only cause much complication, and espe-

cially much labour, because they are only accessible sideways; and they compel the employment of small and consequently expensive chambers. Moreover the contents of chambers with shelves easily become heated, which prevents the turning-out of strong bleach.

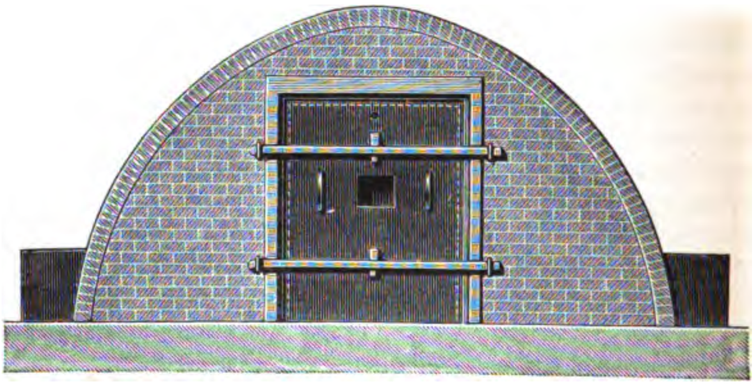
At all (or at least nearly all) large works the stone or wood chambers with shelves have been given up long since (apart from the Deacon process), and have been replaced by large chambers, which permit working inside them, and finishing larger quantities of bleach in one operation. Such chambers are always a little above a man's height, say 6½ feet. It is sometimes stated that they need be only 5 feet high, so that a man may work in them in a bent position: but this would be most reprehensible economy; for the bleach-chamber work, as it is, is so laborious and irksome for the men, that it is out of the question to make it even worse by compelling them to work in a bent position. Even reasons of self-interest, let alone the claims of humanity, forbid this; for the work cannot be properly done in that position. Still less can we approve of making large leaden chambers only 3 feet 3 inches high (as the author himself has seen them in one place); for in these the work can only be done from without.

The *area* of the chambers is now much larger than formerly. Chambers are made 33 feet wide and 66, 80, or even 100 feet long—that is, covering as large a ground-space as vitriol-chambers. It is said that large chambers work more regularly than small ones; at any rate they cause less labour and permit a more complete utilization of the chlorine gas. For turning out one ton of bleach per week a chamber-area of 150 to 180 superficial feet is required; but it is best to have rather more than less chamber-space, so as not to be pressed to open the doors too soon. The cubical contents of chambers without shelves is sometimes stated to be 12½ times that of the chlorine-stills on the old plan (without recovery of manganese).

As for the *material*, chambers of a medium size are made of brickwork, larger ones of lead or sometimes of cast-iron. A brick chamber, such as was frequently met with formerly, is shown in front elevation in fig. 65. It is an elliptical arch, of 13 feet span and 6 feet 6 inches high in the centre, only 4½ inches thick, set with good Portland cement. It can be constructed of good, well-moulded, machine-made, common bricks, since the interior of the chambers must in any case be covered with a coating of cement and painted with tar several times. Small abutments, as shown in the

figure, add to the stability of the arch, which with good cement is very considerable. The two gable walls are put in last; they must be fitted in very tightly, lest they become detached from the arch by settling down. In each gable-end a stone door-frame is put, provided with a rabbet to receive the door. This is sometimes made of two courses of boards crossing each other, with tarred canvas

Fig. 65.



between, and tarred outside; but such wooden doors, even if well made, do not keep gas-tight very long, and have been generally replaced by iron doors of ¼-inch boiler-plate, protected from the action of chlorine by frequently repeated painting with oxide-of-iron paint. The doors are fastened, after plastering the rabbets with lime-putty, each by two horizontal iron bars, the ends of which pass through eyes let into the wall; they are pressed in the centre against the door, and press this against the rabbet. Of course any other way of fastening the doors may be chosen; the most convenient is to hang them on bands. Since in this case their weight is taken off, they may even be made of cast iron. Each door has a hole about 8 inches square to receive a glass pane, on the top a 1-inch hole for letting out the air, and two handles.

The *chamber-floors* are constructed in various ways. Very durable, but very expensive and rarely applied, is a pavement of large stone flags; brick pavements, even of fire-bricks, very soon become uneven and make the bleach impure. Floors made of deals of various descriptions have been tried frequently, but have always failed; so have floors of ordinary cement concrete. But the best

results have been obtained by asphalt concrete, in applying which the same mixtures and apparatus are employed as in asphalting public streets. First a bottom of broken bricks or stones of the size of road-metal is made; upon this the usual mixture of asphalt and sand is cast and perfectly levelled by hot irons. Thus one piece of the floor is finished after the other; and the butt joints are united by partial melting.

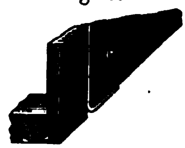
Whilst, for obvious reasons, brick chambers cannot be made much wider than the above-mentioned, no such limit exists for *lead* or *iron* chambers. Chambers made of cast-iron plates, joined by flanges and screw bolts, were at one time the fashion in Lancashire. A good coat or two of oxide-of-iron paint protects them very well from chlorine; and it was expected that they would last almost for ever. But recently they are not in such favour, especially because, in spite of all painting, the bleach is always stained yellow where it comes near the sides. Elsewhere generally lead chambers are employed, made of 5- or 6-lb. lead, similarly to vitriol-chambers, up to 100 feet length and 33 feet width. Such a chamber, cut right through, is shown in fig. 66 in isometrical view.

Fig. 66.


On a properly levelled place a timber framework of sole-trees and crown-trees, *a*, and tenoned-in uprights, *b*, is made. To this are fastened sheets of lead by turning their upper margin round the crown-tree, nailing them to this and by means of straps to the uprights. At the bottom they reach further down than the floor, and are turned inwards 6 or 12 inches, and nailed against the sole-tree. The lead top is hung from joists by means of straps, exactly like a vitriol-chamber (Vol. I. p. 277). In the case of very wide chambers (of

30 feet and upwards), where the top joists would have too great a span, there is a middle row of iron columns placed inside the chamber, carrying a longitudinal girder; all iron and wood is covered with lead. The asphalt bottom is made last, exactly as described above for brick chambers; and in order to keep the joint round the edges tight (which is already facilitated by the lead reaching so far inwards), upright boards, *c*, about 10 inches high, are placed all round the chamber, 2 inches away from the sides, and the space between this and the lead is filled with melted asphalt, forming one mass with the floor itself. This is shown in detail in fig. 67.

Fig. 67.



The doors of lead chambers are made of iron, just like those of brick chambers. Both iron and lead receive three coats of oxide-of-iron paint. If the chambers are in the open air, one side must be made higher than the other, so that the rain can run away in gutters made for that purpose; but the space between the chambers must be roofed in, so that they can be charged or discharged without any interruption arising from the weather.

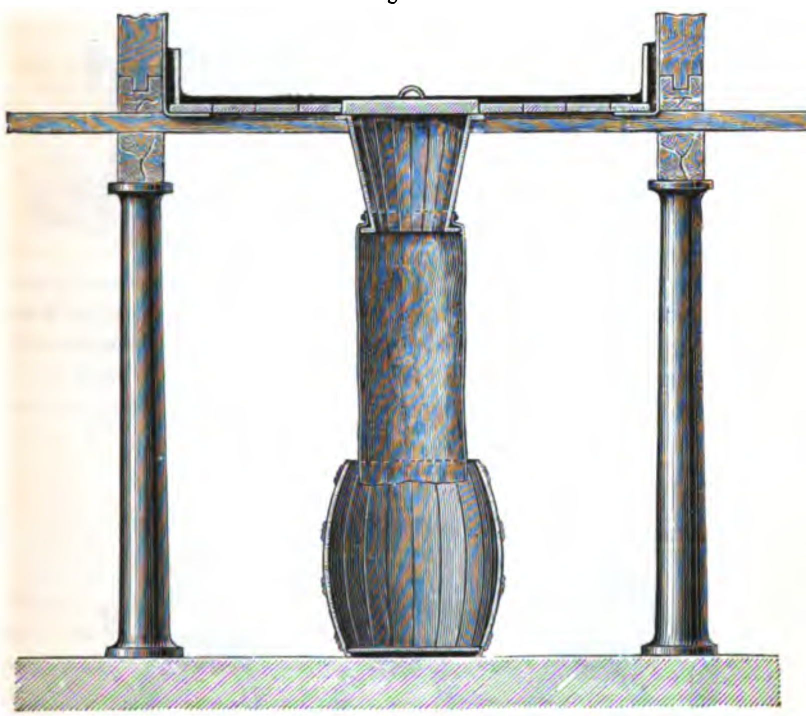
Leaden or iron chambers have this advantage over brick or stone chambers, apart from their larger size, that they better carry off the heat generated in the formation of bleaching-powder, and thus permit pushing the work ahead without the danger of spoiling the bleach by overheating.

Bleach-chambers are usually placed level with the ground; but frequently they rest on *pillars*, with longitudinal sleepers, joists, and flooring, just like vitriol-chambers, leaving an open space of 10 feet height beneath. This space may be used for storing bleach in casks, or lime &c.; but its principal use is to avoid the most unpleasant work in this manufacture, packing into the casks inside the chamber. In this case there are several trap doors in the chamber-floor, each with a wooden hopper attached underneath, from which a canvas tube hangs down, going straight into a cask placed below; through these tubes the finished bleach is pushed down into the casks by means of wooden rakes. (Sometimes stuffing-boxes are provided, in order to employ such rakes for turning over the lime in the absorption-process itself; but these seem now to have been abandoned entirely.)

The arrangement above-described, which can be very much recommended, is shown in fig. 68. It has been noticed that bleach

packed in this way shows ½ to 1 per cent. less than that packed inside the chambers; but it loses so much the less on lying. This can be explained thus:—The larger motion of sliding down into the casks only causes the loss of the most easily decomposed portion, or of mechanically absorbed chlorine gas.

Fig. 68.



All bleach-chambers must have some arrangement for *introducing the gas*. This is always in the roof, and generally consists of a water lute, into which a movable branch pipe can be put from a water lute of the main gas-pipe. There ought also to be separate connecting pipes with water lutes for conveying the gas from one chamber to another. For regular work at least three chambers ought to form a set—the fresh still-gas passing into a nearly finished chamber, the excess-gas into a freshly charged chamber, and, if there are four chambers in the set, again into the third chamber. One chamber must always be cut off—that in which the finished product

is being packed, or which is in course of being recharged. Neill and Smith, in Sept. 1877, obtained provisional protection for an exhauster, which was to convey the gas from one chamber to the other.

Many *other forms of absorbing-apparatus for chlorine* have been tried, but hitherto unsuccessfully. Already in 1816 (according to Richardson and Watts, iii. p. 375) Oberkampf and Widmer proposed revolving cylinders; and this is said to have been the first plan of manufacturing bleach in Germany. It is represented in the sketch fig. 69. The cask A was two-thirds filled with hydrated lime; the chlorine gas entered through the perforated pipe *d*, into which the smaller pipe *e*, coming from the stills, was cemented. The cask rested on the bearings *a* and *b*, and was turned round by a handle at *c*. Another arrangement is said to have been carried out in England, as shown in figs. 70 and 71. A A A are

Fig. 69.

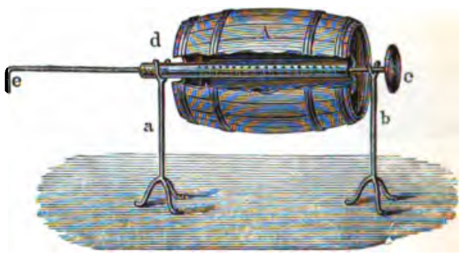
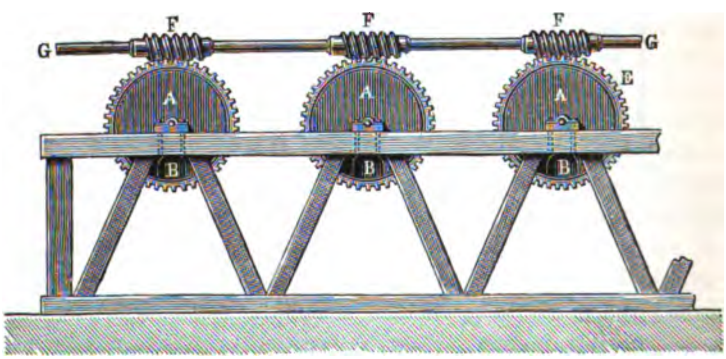


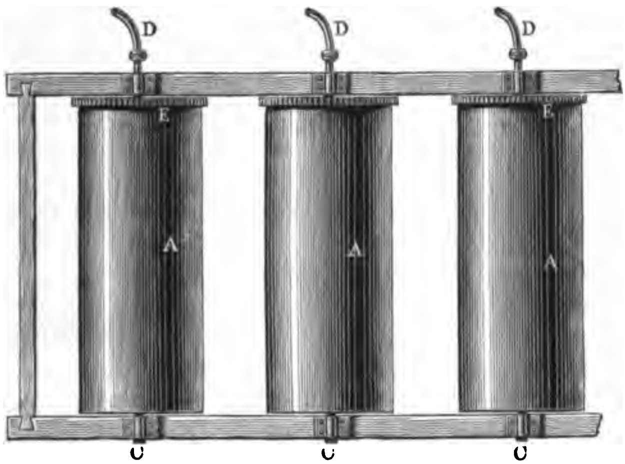

Fig. 70.




cylinders of $\frac{1}{4}$-inch sheet iron, 5 feet in diameter and 13 feet long, coated with cement inside; at one end they have man-holes B B, and are fixed on a wooden frame at such elevation above the ground-floor that the bleaching-powder from them can fall into the packing-casks through a sieve. The axles C C C are hollow and perforated, so that the gas can enter the cylinders; it comes from the stills

through the pipes D D D. The cylinders are made to revolve by the cog-wheels E E and the endless worms F F on the main shaft G. By shifting the worms F F each cylinder can be thrown into or out of gear. The revolutions are slow, 12 or 15 per hour. Each cylinder is charged with about 14 cwt. of calcium hydrate.

Fig. 71.



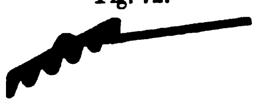

The manufacture of bleach by dropping lime down a tower or shaft, in which chlorine gas ascends, has been proposed several times, *e. g.* by Larkin, Leighton, and White (patent May 20, 1871), and Leather (Sept. 1, 1871), especially for chlorine diluted with air; also by Bramwell and Hargreaves (1877). Bramwell's apparatus has an agitating-shaft inside; Hargreaves's is a vertical cylinder with horizontal shelves, down which the lime is slowly conveyed by means of a central revolving shaft, carrying horizontal arms and scrapers; the lime arrives as finished bleach at the bottom. Cold water circulates in the double walls of the vessel and in the hollow agitator. The apparatus exactly resembles the pyrites-burner (Vol. I. p. 122) and Solvay's soda-drying apparatus (Vol. III. p. 18). The apparatus of Riddel (June 24, 1875) and Malétra (1877) are pretty much the same thing. The latter is a horizontal wrought-iron cylinder, 13 feet long and 6 feet wide, with doors in the sides and below; a central shaft with spirally placed arms and iron blades 10 × 6 inches wide turns the lime round 12 or 20 times per minute. The chlorine gas enters at the top. There are two

openings for allowing the "heat and moisture" to escape [?]. A thermometer serves for controlling the process; in summer too great an elevation of temperature can be avoided by a water-jacket. The finished product falls by the lower door into a bogie. Such a cylinder is to turn out a ton of bleaching-powder in 24 hours.

The inventor claims as an advantage of his process speed of manufacture and uniformity of the product. The author has seen similar apparatus in several places, all standing still, as they would not work after a short run, or because the bleach made in them was too weak.

*The charging of the chambers with lime* is done in the following way. A 3-inch or 4-inch layer of hydrated lime is spread over the floor and levelled; deeper layers cannot be converted into bleach all through. In order to assist absorption, the surface of the lime is "drilled" into furrows by means of a wooden tooth-rake, fig. 72. The lime at the top of the ridges lies about 5 inches, at the bottom 2 or 2½ inches deep.

Fig. 72.



The doors are now put in, and all joints plastered with lime putty, sometimes with the addition of a little salt. Wet clay, which is sometimes used, is less cleanly. Now chlorine gas is admitted; the air-hole in the door is still left open, and is only closed when chlorine issues from it. At first the gas is absorbed very quickly; by looking through the glass panes in the two opposite doors, the gas can be seen descending from the top and losing its green colour near the bottom. If the air has been allowed to get out, there is little fear of any escape of chlorine at this stage. But in time the lime is so far saturated, at first superficially, that it does not absorb the gas so greedily. Some pressure must now be applied to arrest the absorption; and of course special care has to be taken to keep the joints of the doors &c. tight; but, above every thing, the steaming of the stills, which always causes a greater pressure in the chambers, must not be overdone. Besides, too much steaming carries, in spite of long pipes and collectors, steam and acid into the chambers, where they do much harm by forming calcium and chloride and damp lumps; the heating of the chambers by the warm gas is also very injurious. Steam of moderately high pressure (say 40 to 50 lb. to the square inch) is preferable to weaker steam, because there is less condensation of water from it.

The work at this stage is very much facilitated if one chamber is kept ready charged with fresh lime, into which the excess of gas from the first chambers can be carried; then there is much less fear of gas breaking out.

The glass windows are an excellent means of controlling the process, which no one who has been accustomed to them would like to be without. When the chamber becomes very green, no more gas is admitted into it, and a few hours are allowed to elapse, to see whether it still absorbs the gas contained in it. If this is done within a short time, a little more gas must be admitted; but if it takes 12 hours or more before the chamber becomes pale, it is time to open it.

Usually it takes 24 hours before a chamber takes up all the gas it can. If sufficient space is at disposal, so that there is no need to hurry for a few hours (the contrary case involves very great inconveniences), there is no special contrivance necessary for drawing off the gas still contained in the chambers, as it will be gradually absorbed by the lime. In the other case there must be a connexion with the chimney (which is advisable in any case), into which a branch pipe from the chamber can be put in order to air it before it is opened. Where the works are near dwelling-houses much extra care must be taken in opening a chamber, which is rarely done without some gas escaping; there ought to be an absorption-tower fed with milk of lime, into which the chamber-gas can be aspirated before opening the door; or there ought to be at least a connexion with the muriatic-acid-condensers.

After opening the doors the contents of the chamber are examined at once. In any case there will be a superficial crust of bleach; but only with very shallow layers (2 inches) is it possible to get 35 per cent. bleach in one operation.

Testing in the laboratory affords certainty in this respect; but the workmen can judge pretty well by empirical tests whether the bleach is finished or not. The product ought to consist of pretty heavy flakes, not floury, but easily crushed. When a little is taken up on a shovel and thrown off, the powder ought to fall down heavily, not in clouds of dust, which are caused by lime. Kneading a well mixed sample with the fingers ought to make it tough; it will do this only to a very good, strong bleach, which, however, cannot be expected the first time; the bleach at this stage generally tests only from 25 to 30 per cent. available chlorine.

In order to make strong bleach, the contents of the chamber must be turned over with the spade, all lumps crushed, and the stuff lying on the bottom turned upwards. The surface is again dressed into furrows (drilled), the doors are closed, and gas is admitted again. What we have said above about the care necessary in saturating with chlorine holds good here in a higher degree. When the chamber absolutely refuses to absorb any more gas, the latter is cut off, the chamber allowed to rest for 12 or 24 hours to give it a chance of absorbing as much gas as possible, and then opened with the same precautions as the first time. The best plan is to connect the finished chamber with one freshly charged with lime; this gradually draws the chlorine over. As a rule, unless there has been some neglect, the product is now found strong enough for packing—testing at least 36 per cent., as there is always some loss of strength in packing and sampling. But if badly chosen, badly burnt, badly slaked or sifted lime has been employed, if the manganese-ore contains carbonates, if there has been too much steaming and hence sensible quantities of HCl and water have got into the chamber, no strong bleach need be expected. If the strength is found to be only 33 or 34, or even 35 per cent., it will be necessary to turn the stuff again, close the chamber, and give it a little more gas; but if the third time the strength has not got up to 36 per cent., the powder must be packed as it is and sold for what it will fetch; for if a batch saturated with chlorine according to the circumstances is treated with fresh chlorine for some time, it goes back in strength, and that considerably (p. 89). Some workmen think to remedy this by mixing some fresh lime with the powder before admitting fresh gas; the author has never seen much success from this, but has several times got rid of a chamber of 33 or 34 per cent. by bringing another one by special care up to 38 or 39 per ccnt., mixing the contents of both, and packing them together.

In England the bleach is packed as it is; but in France it is usually deprived of lumps by sifting; in this operation it will probably lose a little strength, but will keep all the better afterwards, because it cools completely (see below).

The *packing* of bleaching-powder is a most unpleasant and harassing kind of labour, if it has to be done inside the chamber, not merely from any gas still present, but also from the fine dust arising from the bleach. The men protect themselves from this as much

as possible by a "muzzle" of good flannel in 16 or 24 folds, tied over the mouth and nose up to the ears. Sometimes large sponges are employed instead, or cotton-wool respirators; those filled with a mixture of calcium hydrate and Glauber's salt have not turned out practical; neither does the apparatus of Galibert for breathing in irrespirable gases seem to be used in this case. There are but few men who will undertake "packing;" those who do must always, after a quarter or half hour's work, go into the fresh air, so as to afford some rest to their inflamed eyelids, and to their organs of respiration, which are very much strained in spite of the "muzzle."

The casks for bleaching-powder should be made of dry wood; they are mostly lined with brown paper, and hold 5 or 6 cwt. more if limestone than if cliff has been employed. Their bottoms are covered with plaster, or at least painted with lime. They must be protected both from rain and sunshine; for heating by the direct rays of the sun may cause a sudden, explosion-like decomposition of the bleaching-powder (Hofman & Kunheim, Wagner's Jahresb. 1860, p. 88; 1861, p. 183). In this case oxygen is set free, and the residue consists chiefly of calcium chlorate and chloride. Such cases are extremely rare; but the *slow* decomposition of bleaching-powder in course of time is an unavoidable drawback which will be spoken of hereafter.

Since in no case are all the layers of bleaching-powder of one uniform quality, account must be taken of this on sampling, and still more on packing. The contents of a chamber should be very well mixed, the whole put into a conical heap in the centre of the chamber, and left to itself with closed doors, till the rise of temperature taking place on mixing the different layers has entirely vanished. Packed in this way, the bleach is more durable than when packed immediately after mixing up. Bleach which has been exposed to the rays of the sun before packing is said to keep very badly afterwards. Observations on the decomposing action of the rays of the sun have been made by Riche and by Bobierre (Compt. Rend. lxv. pp. 59 and 803); also by Scheurer-Kestner (see below).

It is very important for making good bleach to avoid a *rise of temperature*. During the absorption of chlorine by lime much heat becomes free; under unfavourable conditions, according to Morin, the temperature rises to 119° C., in which case undoubtedly much chlorate is formed. Berzelius declares even a temperature

of 20° C. to be unfavourable for bleach-making; but this seems exaggerated. Scheurer-Kestner (Compt. Rend. lxv. p. 894) found that sometimes the highest temperature is generated in the top layers, but sometimes the contrary is the case. He affirms that temperatures up to 55° C. are suitable for making strong bleach. With a large excess of chlorine the calcium hydrate gets heated up to 80° or 90° C.; but the product is then already partially decomposing. He asserts that he has found the highest percentage of chlorine just in the warmest (55° C.) places, and hence considers a certain rise of temperature favourable to this process. On Feb. 7, 1877, Cook applied for an English patent for heating the chambers or chlorine-pipes by steam; but even provisional protection was refused for this. According to general experience, and opposed to these last assertions, bleaching-powder is all the better the cooler the chambers can be kept. For this reason lead chambers are superior to stone chambers; and from the same cause it is notoriously much easier to make strong bleach in winter than in summer. In France, on account of the warmer climate, at least in summer no stronger bleach than that containing 30 or, at most, 32 per cent. of available chlorine is made*.

It is also certain that, when the chlorometrical test of bleach has reached its maximum, it is reduced by any excess of chlorine gas admitted to it. We have treated, on p. 708, of the decomposing action of chlorine on bleach and on hypochlorites respectively. Scheurer-Kestner proved by a series of experiments that the top layer of bleaching-powder in the chambers, which is in immediate contact with the gas and should be richest in chlorine, always tests less than the layer immediately below. This, however, may be partly caused by the fact that any HCl carried over would be retained in the top layer. The author once found that 33-per-cent. bleach, which was to be brought up to strength by an excess of chlorine, came down to 27 per cent. The investigations of Hurter

* Mr. Benker, formerly manager of the Petit-Quevilly works near Rouen, informs the author that, in order to avoid a rise of temperature and too much moisture, he mixes his (Weldon) chlorine with 50 per cent. of air, by means of an air-pump, previous to allowing it to act on the lime. In this case no hard crust is formed on the lime, the process goes on very regularly and smoothly, and the strength of the bleach on introducing the new system suddenly rose from 35 to 38 per cent., at which point it is now regularly kept. Probably, besides the reasons mentioned by Mr. Benker, the dilution of the chlorine with air would check the formation of chlorate.

on the absorption of chlorine in the Deacon process should also be compared here.

The *yield of bleaching-powder* from slaked lime ordinarily amounts to once and a half the weight of the latter; but with very good work 166 parts of strongest bleach are obtained from 100 parts of lime as charged. For making a ton of 35-per-cent. bleach very different quantities of manganese are required, depending upon its quality, the way in which the process is carried out, and the tightness of the apparatus. Theoretically bleach of 35 per cent. in the cask, or 36 per cent. in the chamber, only requires 44 per cent. $MnO_2$; *i. e.* 100 parts require 73·5 parts of 60-per-cent. manganese, or 63 parts of 70-per-cent. manganese. But it is considered very good work if only 90 parts of the former, or 75 parts of the latter are used; and the average may be taken as 100 parts of 60-per-cent., or 90 parts of 70-per-cent.-manganese to 100 parts of 35-per-cent. bleach. In Wright's experiments (Chem. News, xvi. 126) the loss of chlorine was about 25 per cent. of that calculated from the manganese. The loss is mostly caused by incompletely dissolving the latter: the chlorine escaping will rarely exceed 5 per cent.; otherwise its smell would be intolerable.

In many works the muriatic acid is not measured, and its quantity varies even more than that of the manganese, because, apart from the causes of loss noticed there, it depends also upon the quality of the manganese and the way of treating it. Theoretically, 100 parts of 36-per-cent. bleach require 74 parts dry HCl, or about 250 muriatic acid of 32° Tw. Practically, rarely less than 400 to 450 parts are used, and relatively even more with weak acid. The French factories, employing small stoneware stills and strong acid, are said to work most advantageously as to muriatic acid. In England, when native manganese is employed, 660 to 700 acid of 28° Tw. are reckoned, upon 100 strongest (39-per-cent.) bleach. In France (according to Payen's Précis, 1877, i. p. 553) 100 parts of muriatic acid of 36° Tw. are said to yield 35 parts of bleach of 110 French degrees=35 per cent. chlorine; but in summer only bleach of 100 degrees=$31\frac{3}{4}$ per cent. chlorine can be made. Favre (Monit. Scient. 1876, p. 276) states that 1000 kilog. of bleach of 110 degrees require only 2220 kilog. acid of 36° Tw.; but this is incredible. His calculation for 1000 kilog. of bleach of 110°, which of course cannot be right as to acid, is as follows:—

| kilog. | francs. |
|---|---|
| 610 slaked lime, @ 3 frs. per 100 kil. ........... | 18·30 |
| 800 manganese (what strength ?) @ 13 frs. per 100 kil. .......... | 104·00 |
| 2200 muriatic acid 22° B. @ 1·9 fr. per 100 kil. . | 41·80 |
| 450 coals @ 3 frs. per 100 kil. .................... | 13·50 |
| Wages .................................... | 19·40 |
| Packages .................................... | 17·50 |
| General expenses and repairs ...................... | 30·00 |
| | 244·50 |

Bleaching-powder ought to be a pure white powder, which in the case of a strong article is mixed with lumps; but these on crushing ought to show just the same properties as the powder; they ought to be completely transformed, and not to contain a core of lime. These lumps are sometimes removed by riddling. In the air bleach gradually attracts moisture and carbonic acid, and finally deliquesces to a pasty mass. It has a peculiar smell, different from that of chlorine, and usually ascribed to hypochlorous acid set free by the carbonic acid of the air; but this cannot be so, as bleach solutions to which an excess of alkali has been added exhale the same smell, even after boiling and cooling in an atmosphere free from carbonic acid (Winkler, Dingl. Journ. cxcviii. 149)*. Mixed with a little water, bleach forms a stiff paste, with a perceptible rise of temperature; if ground up with more water, most of it enters into solution (according to Fresenius first the calcium chloride), but there always remains a considerable residue, chiefly consisting of calcium hydrate, but always containing some bleaching chlorine, which can only be washed out by a very large amount of water. The aqueous solution has a faintly alkaline reaction, the smell of bleaching-powder, and a peculiar astringent taste. This solution is almost exclusively employed in bleaching, as the residue would contaminate the paper-pulp, the fabric, etc., and even locally destroy them. M. F. Hodges has proved that after complete washing the insoluble residue of bleaching-powder is quite harmless.

* According to Phipson (Compt. Rend. lxxxvi. p. 1196), sulphuretted hydrogen passed over bleaching-powder causes the production of a smell of free chlorine: first hypochlorous acid is formed; and this with $H_2S$ decomposes into $H_2O$, S, and Cl.

Bleaching-powder decomposes gradually, even in the absence of air, as is proved by the instance communicated by Hofmann of the explosion of a tightly stoppered bottle, also in well packed and protected casks—but especially under the influence of air and light. Sometimes the decomposition takes place quite suddenly, but only when warm bleach has been packed in hot summer weather. The shaking in a railway truck or a waggon also injures it more than quiet lying in a dark dry place. Hence the strength of bleach is nearly always guaranteed only at the place of shipment; but bleach shipped with 35 per cent. in England ought still to show at Hamburg or New York 33 or at least 32 per cent. Pattinson (Chem. News, xxix. p. 143) examined the speed at which bleaching-powder loses its available chlorine. In the course of 12 months the strength of the following examples of bleach was lowered—

| | $A_1$ | $A_2$ | $A_3$ | $B_1$ | $B_2$ | $B_3$ | $C_1$ | $C_2$ | $C_3$ |
|---|---|---|---|---|---|---|---|---|---|
| from | 28·7 | 37·4 | 37·1 | 32·9 | 35·2 | 36·7 | 31·8 | 37·6 | 37·6 |
| to | 20·8 | 31·2 | 30·2 | 22·2 | 27·9 | 28·0 | 26·4 | 28·2 | 32·3 |

The samples A, B, and C were taken from different works, but the three numbers of each letter from the same chamber in different stages of saturation. The average loss of chlorine in the first three months, from February to April, was 0·33 per cent. per month; from June to September, 0·86 per cent. per month; from November to January, 0·28 per cent. per month. The greatest loss occurred in August, viz. on the average 1·4 per cent. per month. The monthly loss of chlorine on an average of the whole year was *in maximo* 0·90, *in minimo* 0·50, average 0·63 per cent. It is very noteworthy that weak (28·7-per-cent.) bleach lost strength quite as rapidly as the strong (37-per-cent.), which contradicts the formerly general assumption. Pattinson's observations were made with samples kept in loosely corked bottles sheltered from direct sun-light; possibly bleach packed in good casks may behave somewhat differently. Dullo (Wagner's Jahresb. 1865, p. 253) showed that bleaching-powder continually gives off oxygen. at a lower temperature slowly and gradually, at a higher one quickly; but his suggestion (impracticable in any case) that no bleach should be made above 30 per cent., is shown to be useless by Pattinson's experiments.

According to Opl (Dingl. Journ. ccxv. p. 237), bleach yields, when decomposed by heat alone in the absence of moisture,

$$CaOCl_2 = CaO + Cl_2;$$

*i. e.* chlorine is evolved; but in the presence of moisture (which in practice is always present), bleach both in the solid state and in solution decomposes thus:—

$$CaOCl_2 = CaCl_2 + O,$$

but always with simultaneous formation of chlorate, as has long been known [according to the equation

$$6CaOCl_2 = Ca(ClO_3)_2 + 5CaCl_2].$$

(Mr. Schäppi's experiments, quoted above, p. 109, agree with Opl's so far as the action of moist air is concerned, but prove that even in dry air not only CaO and Cl, but also $CaCl_2$, O, and $CaCl_2O_6$ are formed.) The action of light could not be distinguished from that of heat; only in direct sun-light chlorous acid was formed. When bleach decomposes spontaneously under ordinary circumstances, chiefly oxygen is evolved, but little chlorine, and some calcium chlorate. Such a decomposition is caused principally by the bleach spontaneously heating, owing to a mutual reaction of its constituents—not while lying in the chamber, but on being mixed and taken out, as Opl proved by many experiments; this is caused by the fact that in the formation of bleach a migration of the water takes place, and the middle layer becomes poorest in water; on mixing the different layers the compounds $CaOCl_2$ and $CaCl_2$ are hydrated with evolution of heat; so that the temperature of bleach in the casks may rise to 37½° or even 44° C., which quite suffices for explaining its "spontaneous" decomposition, as this commences at 37½°. The formation of calcium chlorate can only occasion a slight evolution of heat. Hence Opl recommends conveying the chlorine gas well cooled into the chambers, employing the lime with as much water as practicable, never allowing the chambers to get warmer than 25°, keeping them very clean, so that no bleach remains in them, and never packing the finished bleach directly into casks, but mixing it well and leaving it in shallow wooden boxes with lids to cool at least to 21° C., turning it over several times before it is packed.

Hurter (Dingl. Journ. ccxxiii. p. 432) noticed only once in ten years, with a weekly make of 100 tons of bleach, a case of considerable heating and decomposition of a cask of bleaching-powder, which he ascribes to an accidental admixture of organic substances.

Wright and Kingzett ascribe the explosive properties of bleaching-powder to an admixture of a manganese-salt (Chemical Society's Meeting of March 20th, 1879).

# CHAPTER IV.

## OTHER PROCESSES FOR MANUFACTURING CHLORINE.

The numerous proposals for producing chlorine in another way than by decomposing manganese-ore (or artificially recovered manganese peroxide) with hydrochloric acid will now be enumerated; but it should be stated at once that only two of them, the process of Dunlop and that of Deacon have had a permanent success. That of Dunlop is, by the necessity of generating at the same time nitrous acid, restricted to such a narrow field that it has only been carried out at St. Rollox. That of Deacon will be treated in detail in a separate chapter.

*Chlorine by Electricity.*—C. Watt, on Sept. 25th, 1851, patented the decomposition of hydrochloric acid, or of potassium chloride and sulphuric acid, by the galvanic current; the hydrogen formed at the same time was to serve as fuel. The chlorine evolved was to be immediately conducted into an alkaline solution, and, according to the temperature, hypochlorite or chloride made by it. Dickson, on July 17th, 1862, patented something quite similar, and on Aug. 13th of the same year obtained provisional protection for the electrolysis of sodium chloride, this time with the addition that the decomposition was to be assisted by nitric, nitrous, sulphurous, or sulphuric acid, ferrous or ferric chloride, cuprous or cupric chloride, ferric or cupric oxide, or by passing oxygen obtained by electrolysis through certain ignited chlorides, or by the galvanic decomposition of fused common salt. This medley requires no criticism. Even on May 6th, 1872, Fitzgerald and Molloy again patented the electrolysis of a solution of common salt by means of electrodes of coke impregnated with paraffine. The reporter in the

'Berichte der deutschen chemischen Gesellschaft' (vi. p. 1141) states, quite seriously, that this process was being applied to sea-water at some sea-side place, *e. g.* at St. Lawrence near Margate, on a large scale and with prospects of success; but otherwise nothing has become known of this wonderful story.

*Chlorine from Aqua regia.*—Baggs and Simpson (prov. prot. Sept. 21, 1864) heat hydrochloric and nitric acids together, pass the evolved chloro-nitric and chloro-nitrous gas through oil of vitriol, where the nitrous acid is retained and chlorine is liberated in order to be used in the ordinary way. The nitrous vitriol is decomposed by dilution with water and agitation, and the nitrous gas evolved is reconverted into nitric acid by the action of air; the vitriol is concentrated by evaporation and used over again. Tessié du Motay treats cuprous chloride with aqua regia; this yields cupric chloride, both of which are to be utilized in the manner to be described below.

*Chlorine by the assistance of Nitrate.*—Dunlop patented (March 16, 1847) the preparation of chlorine along with nitrous acid and sodium sulphate by heating together common salt, nitrate of soda, and sulphuric acid. The muriatic acid formed at the same time is washed out by water, after the nitrous acid has been absorbed by concentrated vitriol. This process has been already described (Vol. I. p. 320). It has been carried out at St. Rollox, and is still being worked there (comp. also Vol. II. p. 20). Precisely the same thing was patented by Roberts and Dale on Oct. 8, 1858. Binks (Feb. 8, 1839) patented the preparation of chlorine by passing 4 vols. of HCl gas, along with 1 vol. of the gas given off on heating sodium nitrate to a red heat, through red-hot stoneware pipes; a mixture of chlorine, nitrogen, and water is obtained, which is purified from the undecomposed HCl by washing with water. In the same way from 1 vol. HCl and 2 vols. $CO_2$ there is to be obtained chlorine, carbon monoxide, and water.

Tessié du Motay (Bull. Soc. Chim. xxii. p. 48) passes the gases evolved on heating NaCl, $NaNO_3$, and $SO_4H_2$ through cuprous chloride. $CuCl_2$ and NO are formed; the latter is to be mixed with hydrogen and converted into ammonia by red-hot platinized pumice; by heating the $CuCl_2$ to 200° or 300° it is to be decomposed into $Cu_2Cl_2$ and Cl (comp. Mallet's process).

*Chlorine by the assistance of Nitric Acid and Manganese.*—Schlösing (Compt. Rend. lv. p. 284) noticed that, by the action of a

mixture of nitric and hydrochloric acids on manganese peroxide at a certain degree of concentration, chlorine is evolved, mixed with the reddish products from aqua regia; but at lower concentrations, even at a boiling heat chlorine alone escapes and manganous nitrate remains behind. If the latter be calcined, $MnO_2$ remains behind, and the escaping ruddy vapours can be reconverted into nitric acid by the action of water and air: thus both materials are recovered and can be used again. The best proportions are:—4 equivalents of nitric acid containing 505 grams $N_2O_5$ per litre, and 3 equivalents of hydrochloric acid containing 397 grams per litre; to the mixture one seventh of its bulk of water is added, and the whole heated in a calcium chloride bath up to 122° C. Schlösing in this way obtained in two experiments 96 and 90 per cent. of the calculated quantity of chlorine; but the heating at first should not be too strong. The decomposition of manganous nitrate commences at 150°, and regularly goes on at 175° or 180°; at 195° C. it is most vigorous. The remaining oxide is pretty hard and close, and contains up to 93·3 per cent. $MnO_2$, along with a little lime and iron*. Neither N nor NO are formed; and thus the complete recovery of the nitric acid depends only upon the completeness of the decomposition. On a small scale Schlösing obtained an acid of 62° Tw. and only lost 9 per cent. This process has never got beyond the laboratory stage; but it deserved more attention, at any rate before Weldon's process had been worked out, especially as in it, as well as in Dunlop's very similar process, *all* the chlorine of the hydrochloric acid is obtained as such:

$$MnO_2 + 2NO_3H + 2HCl = Mn(NO_3)_2 + 2H_2O + 2Cl.$$

*Chlorine by Permanganates.*—Condy obtained provisional protection (Dec. 28, 1866) for the evolution of chlorine from a mixture of common salt, sodium permanganate, and sulphuric acid; the latter was gradually to be added to the mixture. This process was to be employed chiefly for disinfecting, but also for manufacturing-purposes when quite pure chlorine was required.

* According to Gorgeu (Compt. Rend. lxxxviii. p. 796) crystals of manganese dioxide are obtained resembling entirely the mineral polianite (p. 114) in hardness, specific gravity, colour, and streak, by slowly heating manganous nitrate to 155°–162° C. and keeping it at that temperature for 24 hours. The product contains 36·5 to 36·75 per cent. of oxygen.

Similar to this are the patents of Tilghman (Feb. 1st, 1847) for employing magnesium chloride with manganese peroxide or permanganates, and that of de Sussex, taken out almost at the same time.

Recently Tessié du Motay has taken up the employment of permanganates for the manufacture of chlorine (Wagner's Jahresb. 1871, p. 255; 1873, p. 270). He passes a current of HCl into a dark-red-hot retort filled with a mixture of manganese peroxide and lime. Cl and $H_2O$ escape; MnO and $CaCl_2$ remain behind. The chlorine is utilized in the ordinary way; over the residue a current of air is passed at the same temperature as before; thus the chlorine contained in the $CaCl_2$ or $MnCl_2$ becomes free and escapes, mixed with N and air in excess. The gases are passed into receivers containing a mixture of CaO and MnO (made by decomposing $MnCl_2$ with an excess of lime); here hydrated $MnO_2$, bleaching-powder, and $CaCl_2$ are formed. This mixture is treated with HCl in the usual way, and the evolved chlorine passed into bleach-chambers. In the receivers a mixture of $MnCl_2$ and $CaCl_2$ remains behind, which is treated with lime, and this again converted into a mixture of MnO and CaO (both hydrated). The $CaCl_2$ yielded in the different operations is treated with magnesium carbonate, and the $MgCl_2$ heated so as to obtain HCl from it. The inventor asserts that, 1st, the manganese oxides are continually regenerated; 2nd, all the chlorine of the hydrochloric acid is obtained; and, 3rd, all the chlorine is obtained in a pure state. This would be excellent if it were true; but few people will believe it.

*Chlorine from Chromates and Hydrochloric Acid.*—MacDougal and Rawson, on Nov. 21, 1848, patented the manufacture of chlorine by heating chromates or bichromates, preferably those of calcium, with hydrochloric acid, either in the free or the nascent state. The residue of mixed chlorides and chromium salt is treated with nitric acid, the HCl distilled off, and the residue heated further; the chromate is thus regenerated, and nitrous gases are evolved, from which nitric acid is recovered by the action of air and water. Peligot (Ann. Chim. Phys. [2] lii. p. 267) and Gentele (Dingl. Journ. cxxv. p. 492) recommended this process. They employed the compound $2KCl,Cr_2O_6$, discovered by Peligot, which on heating to 100° gives off its chlorine almost entirely (Wagner's Jahresb. 1861, p. 177). The application of calcium chromate was patented by Shanks (Sept. 7, 1858) with the addition of re-

covering the chromates in a cheaper way. Starting from calcium chromate and hydrochloric acid, there are formed calcium chloride, chromic chloride, water, and chlorine, thus:—

$$2CaCrO_4 + 16HCl = 2CaCl_2 + Cr_2Cl_6 + 8H_2O + 6Cl.$$

Half of the chlorine escapes without, the other half is driven off by heating; this can be done in the ordinary chlorine-stills. The grass-green solution is neutralized with lime, and by more lime all chromium precipitated as hydroxide:

$$Cr_2Cl_6 + 3Ca(OH)_2 = Cr_2(OH)_6 + 3CaCl_2.$$

Another two molecules of calcium hydrate are added, and the precipitate collected on a filter; the solution of $CaCl_2$ runs away; and the mixture of chromium oxide and lime is calcined in a reverberatory furnace at a dark-red heat with access of air; oxygen is absorbed, and calcium chromate regenerated, thus:—

$$Cr_2O_3 + 2CaO + 3O = 2CaCrO_4.$$

The chromium oxide thus acts as mediator between the atmospheric oxygen and the hydrogen of HCl; in this way the manganese-ore was to be entirely done away with. But theoretically from 16 molecules of HCl only 6 atoms chlorine are obtained, whilst by means of $MnO_2$ 8 atoms Cl would be got; the excess of HCl practically required is no less in the first case than in the second. This is the first great drawback; but it is very doubtful whether the cost of precipitating by lime, filtering, and calcining does not exceed that of fresh manganese; and in no case can a competition with the Weldon process be thought of. In fact Shanks's process, after working a short time, was given up again.

Another process for the recovery of the chromates was proposed by Claus (pat. No. 1054, Apr. 8, 1867). The mixed solutions of calcium and chromium are evaporated to dryness in a reverberatory furnace with a brick hearth, and the residuary mass heated with admission of air at a temperature somewhat below the fusing-point of calcium chloride—say, between the melting-points of lead and zinc. Thus calcium chromate is recovered and hydrochloric acid and chlorine escape mixed with other gases. The hydrochloric acid is washed out in a coke-tower; and the chlorine is retained in another tower by a stream of water holding hydrated lime or magnesia in suspension. The hypochlorides thus formed are utilized for generating chlorine by means of hydrochloric acid, or, less advan-

tageously, for converting chromium chloride into chromate. If magnesia be employed, the magnesium chloride formed is decomposed by heat into hydrochloric acid and magnesia. The most obvious difficulties of this process are the evaporation of the acid liquors in a brick furnace and the complete conversion of the chromium chloride into chromate.

Aubertin (Bauer, Chem. Grossindustrie, 1873, p. 17) proposes manufacturing chlorine by passing air and HCl gas over red-hot potassium bichromate.

*Chlorine from Magnesium Chloride and Manganese.*—Tilghman (pat. Feb. 1, 1847) heats $MgCl_2$ with dry manganese-ore or with permanganates. Only a week later De Sussex patented the same process, with the proviso that sulphuric acid might also be added; the mixed manganese and magnesium sulphate were to be worked up in a complicated way. Instead of magnesium chloride aluminum chloride might be employed.—The same principle underlies Ramon de Luna's proposal (Compt. Rend. xli. p. 95) to employ a mixture of magnesium sulphate, common salt, and manganese; the following reaction takes place:—

$$2MgSO_4,H_2O + 4NaCl + MnO_2 = 2Na_2SO_4 + MnCl_2 + 2MgO + 2H_2O + 2Cl.$$

This is also mentioned in the patent of Binks and Macqueen (May 19, 1860). A similar process was again recommended by Clemm (Dingl. Journ. clxxiii. p. 127). Crude $MgCl_2$ liquor (from the Stassfurt mines) was to be evaporated to 88° Tw., and mixed at a higher temperature with so much ground manganese that 1 mol. $MnO_2$ would be present for every 2 mols. $MgCl_2$. The cooled and solidified mixture is crushed and exposed in large stone chambers to the action of steam superheated to 300° C. or upwards; chlorine gas is evolved, is purified from steam and HCl by an apparatus filled with manganese, and passes into a small gas-holder made of wood or gutta-percha, etc., which serves as collector or regulator before the gas passes into the absorbing-apparatus. This process has never become practical; as to the way in which Weldon employs it in his magnesia process, we refer to the detailed description of the latter in Chapter VI.

*Chlorine by heating the Chlorides of Manganese, Iron, Zinc, or Calcium with Manganese Peroxide and Sulphuric Acid.*—This was patented by Binks (prov. prot. May 28, 1853). Ferric chloride

especially is used by several others, without adding $MnO_2$. Barrow (Feb. 26, 1856) patented the manufacture of chlorine by heating dry manganous chloride in a current of dry air.

*The Decomposition of Hydrochloric Acid by Atmospheric Air* was first patented by Oxland (Feb. 20, 1840); the mixture of the two gases is passed through red-hot pumice, then cooled and the unchanged HCl washed out by water.

Jullion (patent Oct. 22, 1846) passes HCl and oxygen gas through heated platinum sponge, and washes the chlorine gas with water. Binks (prov. prot. June 28, 1860) decomposes HCl by atmospheric oxygen at a high temperature in the presence of a substance retaining the water but not the chlorine. On May 17, 1862, he again applied for a patent for the same thing, adding to it the employment of concentrated vitriol; and once more, on Nov. 17th, 1862, without any essential novelty.

Dufrené obtained provisional protection (July 11, 1865) for obtaining chlorine by passing dry HCl and air over red-hot pumice; inversely a mixture of chlorine and steam under like circumstances was to yield HCl and oxygen gas (which seems to have been his principal object); the nitrogen gas obtained in either case to be "passed over red-hot iron in a spongy state, by which the azote is absorbed; when hydrogen is brought on the combination of azote and iron thus formed, the decomposition is immediate, and a large quantity of ammonia is produced" (*sic*).

Henderson (patent of Nov. 15th, 1871) passes a mixture of HCl and air over bricks or blocks of ferric chloride, made plastic by a little clay, heated to 200°. Or the HCl can first be passed over the oxide till it is saturated, and then heated air admitted, which again oxidizes the iron and liberates chlorine. The latter is brought into contact with fine lime-dust in revolving cylinders. This process is founded upon the same reactions as those of Longmaid, Macfarlane, and Königs, but adds the *constant* action of ferric oxide, which is only the carrier of the reaction; and, on the other hand, it has analogy with the processes employing cuprous chloride and those with porous indifferent bodies in a red-hot state, among which it is enumerated in this place.

Weldon (patent of Aug. 27th, 1871) passes a mixture of HCl vapour and atmospheric air over platinized asbestos or another platinized porous substance.

Wigg (prov. prot. May 12, 1873) proposes pumice, Townsend

(patent of Oct. 10, 1874) manganese or magnesia compounds, for the same object. The process of Aubertin, mentioned on p. 181, might also be cited here.

*Chlorine by Ferrous Chloride and Air.*—Thibierge (patent, Oct. 13, 1855) passes dry HCl gas over heated iron, and conveys the hydrogen gas formed into a gas-holder. The $FeCl_2$ is exposed in the same vessel to the action of a current of dry air, and by this decomposed into ferric oxide and chlorine.

The same action is also utilized in the patent of Macfarlane of 1863 (compare this); on it also are based those of Longmaid, Königs, Henderson, and others. It was patented once more as novel by Larkins, Leighton, and White on May 20th, 1871.

*Chlorine from Hydrochloric Acid and Atmospheric Air by the mediation of Cuprous Chloride.*—Vogel (Dingl. Journ. cxxxvi. p. 237) in 1855 proposed evolving chlorine from cupric chloride by heating it to an incipient red heat:

$$2\,CuCl_2 = Cu_2Cl_2 + 2\,Cl.$$

The cuprous chloride is mixed with hydrochloric acid, and, by the atmospheric oxygen, converted first into oxychloride ($CuCl_2,3CuO, 3H_2O$) and then again into cupric chloride:

$$Cu_2Cl_2 + 2\,HCl + O = 2\,CuCl_2 + H_2O.$$

But on working on a large scale not half, but only one third of the chlorine of $CuCl_2$ is said to be obtained, viz. 13·8 per cent. of the latter. According to Hoffmann's Report by the Juries, 1862, p. 35, Gatty examined the above proposal, and found that the chlorides of copper quickly corrode stoneware vessels and the hardest fire-bricks, so that hardly any vessels can be made for evaporating and calcining them. This manipulation is very dangerous to the health of the men; and even a small loss of copper, considering its high price, would make the process economically impossible.

Laurent patented just the same process as novel on Jan. 21, 1860. Cupric chloride is made by dissolving CuO in HCl, or Cu in aqua regia, or precipitating a solution of $CuSO_4$ by $BaCl_2$ or $CaCl_2$; the solution is dried down and heated at 100° or 150° C. till the water is given off and a brownish-yellow powder remains; this is mixed with half its weight of sand, and kept heated in a retort to 220° or 300° C. till half of the chlorine contained in the cupric

chloride has been driven off. The remaining mixture of cuprous chloride and sand is mixed with hydrochloric acid and evaporated in a current of air; hydrated cupric chloride is obtained by crystallization, and heated with or without sand in order to drive off the water and begin the process anew. This process possesses a certain importance, because it may be considered one of the precursors of Deacon's process. On Jan. 1, 1864, Trégomain patented the same process with unimportant modifications: he fuses the cuprous chloride, grinds it, converts it into oxychloride in a current of air, treats this with liquid or gaseous HCl, and obtains the $CuCl_2$ formed by lixiviation and crystallization.

A new patent was taken by Mallet (Dec. 3, 1866) for converting cuprous chloride by oxygen into oxychloride, which gives off its oxygen at a dark-red heat and is again converted into cuprous chloride. He employs horizontal cylindrical cast-iron retorts, lined with an enamel not acted upon by the chlorides of copper, *e. g.* copper borate, silicate, or phosphate. The retorts have a discharging-aperture at the bottom; and in the elongation of their axis there is an exit-tube; they are placed in a furnace on rollers, which permit their rotation round their axis. The oxychloride is mixed with 15 to 20 per cent. of inert material, such as china-clay, sand, porcelain, or powdered fire-bricks; and the mixture always remains within the retort when in regular working. When oxygen alone is required, only a dark-red heat is applied. When gas has ceased to be evolved the retorts are cooled down and jets of steam and air directed into them while they are rotating, so that in two or three hours the oxychloride is regenerated. If, however, HCl gas is injected from the first, or if to the oxychloride formed at first HCl is added, cupric chloride is produced, from which chlorine can be obtained by heating. 100 kilog. of $CuCl_2$ are stated to yield 6 or 7 cubic metres of chlorine gas; and as in 24 hours at least 4 or 5 operations can be performed, the above quantity suffices for a daily production of from 4 to 6 cwt. of bleaching-powder. The further development of these reactions will be described in Chapter VII., along with the Deacon process.

*The Production of Chlorine by calcining Sulphurous Ores with Chlorides in the presence of an Excess of Air, i. e.* at the same time with $SO_2$ and $SO_3$, is the subject of many patents which have for their object the simultaneous utilization of sulphur. They have accordingly been mentioned in treating of sulphuric acid and of

sulphate. Longmaid's patent of Aug. 4, 1845, proposes at the same time to produce metallic oxides and chlorine by *calcining the chlorides* of manganese, copper, iron, zinc, or lead *with an excess of air.*

Swindells and Nicholson (patent, Oct. 14, 1852) obtain chlorine by passing oxygen or air over heated manganous or ferric chloride. Robinson (prov. prot. Jan. 12, 1860) produces chlorine by treating red lead with hydrochloric acid; the $PbCl_2$ is to be converted into $PbCO_3$ by the solution of a carbonate (preferably that of ammonium), and the lead carbonate to be utilized as such or converted into red lead by heating. Macfarlane (patent, Jan. 14, 1863) mixes 6 cwt. dried copperas with 4½ cwt. of decrepitated common salt and 1½ cwt. ferric oxide, heats the mixture in a muffle furnace in a current of air dried by quicklime, and thus obtains sodium sulphate, ferrous and ferric chlorides; the latter are converted by the dry air into ferric oxide and chlorine. The chlorine is drawn by an exhauster through purifiers (boxes lined with lead and containing moistened pieces of coke) into wooden absorbing-boxes charged with slaked lime. The residual mixture of sodium sulphate and ferric oxide is mixed with 214 lb. of coal and smelted in a reverberatory furnace, the bottom of which has been lined with a mixture of ground quicklime and basic slag. The fused mass is lixiviated, the green solution decolorized by heating in the presence of gases rich in carbonic acid, and the solution of sodium carbonate worked up in the usual manner. The iron sulphide undissolved is to be converted into ferrous sulphate by the action of moisture and air [which is well known *not* to happen], and the ferrous sulphate obtained by dissolving and crystallizing. This part of the process is a modification of Malherbe's soda-process, afterwards taken up again by Kopp. The same process emerges once more in a patent of Königs (May 15, 1871): he moulds dried pyrites, common salt, ferric oxide, and water into bricks, which are dried and heated in a current of air—essentially Longmaid's process. Even in 1872 Kenyon and Swindells patented the production of chlorine along with sulphuric acid from a mixture of rock-salt, sulphur, iron- or copper-pyrites, and a little nitrate of soda. Although the production of chlorine in the calcination of sulphurets with chlorides has long since been explained by the previous formation of sulphuric anhydride and its action on HCl or chlorides in the presence of air, Deacon patented that reaction as a novel one (July 21, 1871).

Lalande and Prud'homme (Bull. Soc. Chim. 1872, p. 7; 1873, p. 74) generalized the reactions employed in Longmaid's process, by working not only with sulphuric anhydride, but also with *silica, boric, stannic, phosphoric acid,* and *alumina.* If, for instance, dry air is passed over a red-hot mixture of silica with the chloride of an alkaline or earthy metal, chlorine is liberated and a silicate of that metal is formed:

$$2\,NaCl + SiO_2 + O = Na_2SiO_3 + 2\,Cl.$$

If HCl gas is passed over the ignited mixture along with O or air, the silicate is always decomposed again, the chloride regenerated, and chlorine continuously given off. The aqueous vapour formed gives rise to secondary reactions: it is decomposed by chlorine into oxygen and hydrochloric acid; it also decomposes the chlorides at a red heat into oxides and HCl. Between the quantities of chlorine, aqueous vapour, and hydrochloric acid which issue from the apparatus a state of equilibrium is probably produced; so that the quantity of chlorine in proportion to that of HCl cannot surpass a certain maximum, which for lower degrees of temperature is probably a higher one. Pumice and broken bricks have a similar effect upon the liberation of chlorine as those acids, but not pipeclay. The authors state that in their experiments they obtained as much chlorine as Deacon in his process with marbles saturated with cupric sulphate; but in the latter case the reaction takes place at a lower temperature.

Solvay (patent, Jan. 8 and 12, 1877) also liberates chlorine from calcium or magnesium chloride by means of silica, alumina, or clay. The substances are mixed, dried, and exposed to a current of dry air at an intense heat. The employment of the residual silicates and aluminates has been mentioned in the chapter treating of the ammoniacal soda-manufacture. Solvay also proposes reconverting the silicates and aluminates by liquid or gaseous HCl into chlorides, and producing chlorine from these by the action of hot air (compare Vol. II. p. 172, and Vol. III. p. 31).

*Chlorine from Hydrochloric Acid and Air by means of Chromic Oxide* (Hargreaves and Robinson's patent, Feb. 17, 1872).—Sodium or potassium chloride is intimately mixed with chromic oxide, or with manganic oxide, and moulded into bricks. After drying, these are loosely stacked in chambers heated from without and brought to a red heat. By passing heated air over them chlorine is libe-

rated, or hydrochloric acid by air mixed with steam. The best mixture is 2 or 3 parts of $Cr_2O_3$ to 1 part of NaCl. Instead of heating the chambers from without, the action may be produced by an additional heating of the entering air, the chambers being surrounded by bad conductors, *e. g.* magnesia bricks.

A general investigation of the mutual action of hydrochloric acid and oxygen in the presence of certain metallic compounds has been made by Lamy (Bull. Soc. Chim. 1873, vol. xx. p. 2). His results are as follows:—1st. All compounds of copper, iron, manganese, and chromium, and all compounds containing only traces of these elements, as pumice, porcelain, silica, glass, always yield a current of chlorine if they are heated and a mixture of hydrochloric acid and oxygen or air is passed over them. 2nd. The yield of chlorine in proportion to the HCl employed is dependent upon the nature of the active substance, the temperature, the composition of the gaseous mixture, and the rapidity of the gaseous current. 3rd. If oxides or chlorides are not employed directly, the salts are decomposed; *e. g.* cupric sulphate yields first oxide, then chloride. 4th. The quantity of the oxide liberated or the chloride formed is very slight in proportion to the quantity of chlorine gas produced. 5th. Under like conditions the yield of chlorine decreases as the rapidity of the gaseous current increases. 6th. On employing copper-salts the decomposition is at its maximum at about 440° C. At this temperature and with mixtures of HCl and O or air which contain from 60 down to 4 per cent. of HCl, the yield of chlorine varies from 20 to 95 [?] per cent. At the temperature of boiling mercury no chlorine is evolved. 7th. Under like conditions the oxides of manganese, iron, or chromium yield only half as much chlorine as copper; but at a low red heat or near the melting-point of glass the yield of chlorine is 50 to 75 per cent. $Mn_2O_3$ yields more chlorine than $Fe_2O_3$; the chlorides of the former are also less volatile. 8th. Common pumice at 350° C. yields no chlorine, at 440° C. 15 per cent., at a red heat 30 per cent. When purified from iron by hydrochloric acid, it yields extremely little chlorine. 9th. Porcelain, apparently pure silica, Bohemian glass, and alkaline chlorides (impure) yield only a small percentage of chlorine at the heat of fusion of glass, ferric chloride being volatilized.

# CHAPTER V.

## THE UTILIZATION OF STILL-LIQUOR.

The "still-liquor" produced in the ordinary chlorine-manufacturing process contains chiefly manganous chloride, together with ferric chloride and the chlorides of any other metals occurring in the manganese-ore, and also a considerable quantity of free hydrochloric acid and free chlorine. In daily practice it is tested for *free acid* by a very simple and sufficiently accurate plan. To a certain volume of the still-liquor normal caustic soda is run in from a burette till flakes of ferric hydroxide are formed which do not dissolve again; these indicate the saturation of the free acid. When the stills are heated by direct steam the liquid rarely contains less than 5 per cent. free HCl; it mostly contains 6 per cent., and with bad work 10 per cent. and upwards, *i. e.* far more than one half of the total Cl present as free HCl. The liquor at Dieuze had, according to Hófmann, the following average composition:—

| | |
|---|---|
| Manganous chloride | 22·00 |
| Ferric " | 5·50 |
| Barium " | 1·06 |
| Free chlorine | 0·09 |
| Hydrochloric acid | 6·80 |
| Water | 64·55 |
| | 100·00 |

Black (Transactions of the Tyne Social Chemical Society) gives the following analysis of still-liquor obtained with native manganese:—

| | | | |
|---|---|---|---|
| HCl .............. | 6·6220 | = 6·622 | per cent. HCl. |
| $Al_2Cl_6$.............. | 0·6200 | = 0·500 | „ „ |
| $MnCl_2$ ........... | 10·5700 | = 6·120 | „ „ |
| $Fe_2Cl_6$ ........... | 0·4551 | = 0·310 | „ „ |
| $H_2O$ .............. | 81·7329 | | |
| | 100·0000 | 13·552 | |

Hence, of 13·552 HCl found, only 6·120, *i. e.* 45 per cent., was combined with manganese. Now, even if all the Mn had been originally present as $MnO_2$, only an equal quantity (6·120) of HCl had escaped as chlorine; so that the total HCl originally employed amounted to 19·672. Accordingly the HCl usefully employed was only 62·2, that combined with iron and aluminium 4·1, and that found free 33·6 per cent, of the whole.

The acid still-liquor has always been a source of great embarrassment to the producers of chlorine. On running-off the stills it causes a fearfully suffocating smell of chlorine, which in the case of large quantities is perceptible at distances of half a mile and upwards; in the watercourses into which it is discharged it destroys all fish, it damages the foundations of buildings, quays, and bridges, &c.* Moreover all manganese contained in it is lost. Hence very many proposals have been made for utilizing the still-liquors, partly only with a view to employing the free acid, partly for making the manganese available in some shape, and partly for regenerating $MnO_2$ from them. Of all these, only Dunlop's and Weldon's recovery processes have been practically successful, the latter certainly to a surprising extent. Whilst the price of manganese in 1871–73 had risen to twice its former figure, it has, in consequence of the general introduction of Weldon's process, receded so far that many mines have had to stop working.

*Utilization of the Manganese in Still-liquor.*—Apart from the

* From experiments made by Weigelt (Chemiker-Zeitung, 1880, p. 39), on behalf of the Government of Elsass-Lorraine, it appears that trout were killed by 5 minutes' stay in water containing 0·005 gram of chlorine per litre, or by a prolonged stay in water containing 0·002 gram of chlorine per litre, whilst they did not seem to be affected by a 15-minutes stay in water containing 3 grams of sodium carbonate, or calcium chloride, or sodium chloride per litre. Sulphuric acid proved to be far more injurious to trout than hydrochloric acid. The numerical results found in the case of trout should not be generalized, since this kind of fish is more than usually sensitive to impurity of the water.

recovery of $MnO_2$, the most important effort of this kind was Laming's patent (Mar. 4, 1847; comp. also that of June 20, 1859) for *purifying coal-gas* from the $H_2S$ contained therein. For this purpose considerable quantities of manganous chloride were made from still-liquor and converted into $MnCO_3$ by chalk or gas-water. This process, however, was abandoned for that employing bog-iron-ore, although Laming, according to his later patent, made $Mn(OH)_2$, and regenerated the MnS in just the same way as the oxide of iron employed in purifying coal-gas. Dales employs the still-liquor for disinfecting (patent, Sept. 22, 1859); and many others do the same thing. Lunge (patent, April 20, 1866) and Weldon (in various patents) employ a mixture of $MnCl_2$ and lime for absorbing $H_2S$.

The addition of the manganese of still-liquor has often been proposed for *improving iron-ores*, especially for steel-making, *e.g.* by Hunt (prov. prot. Jan. 12, 1855), by Henderson (Dec. 24, 1862), especially also by Schaffner (Wagner's Jahresb. 1868, p. 225), who precipitated the still-liquor by lime, calcined the mixed oxides in a reverberatory furnace, and employed the $Mn_3O_4$, containing iron, as part of the charge of a blast-furnace. By this process the product of certain blast-furnaces is said to have become fit for the Bessemer process, by combining it with a little manganese. Crockford (patent, July 25, 1863) proposes to employ the precipitate produced in still-liquors by lime as a colour. Leykauf (Dingl. Journ. cxc. p. 70) also makes a colour from still-liquor by fusing the dried product with phosphoric acid, boiling with ammonia, filtering, drying down the filtrate, fusing again, and exhausting with boiling water; the colouring matter, which he called "Nuremberg purple," remained behind. In *glass-making* the still-liquor, after precipitation with lime, has been employed as a cheap substitute for manganese-ore. Only quite locally (in Alsace) can the still-liquor be sufficiently utilized by making from it crystallized manganous chloride, which is employed for manufacturing "*bistre*" in calico-print works.

Gossage (patent, Nov. 8, 1856) makes from it manganous carbonate for the purpose of *decomposing* sodium sulphide, and thus producing soda ash.

An interesting employment of manganous chloride from still-liquor is, to make *barium chloride* from the sulphate as a preventive against steam-boiler scale, and for producing "permanent white."

This process seems to have been invented by Kuhlmann (Compt. Rend. xlvii. p. 164); the patent taken by Clark on Nov. 11, 1856, as a communication from abroad, probably belongs to Kuhlmann. The same process forms the subject of a provisional protection obtained by Seitz (Aug. 6, 1860). The free acid is saturated by barium or calcium carbonate, the liquid run into a furnace charged with a mixture of ground sulphate of baryta and coals, and the mixture heated for several hours in a reverberatory furnace, where barium chloride and manganese sulphide remain behind, and carbon monoxide burns away:

$$BaSO_4 + MnCl_2 + 4\,C = BaCl_2 + MnS + 4\,CO.$$

The two former are separated by lixiviation, and the barium chloride obtained by evaporation and crystallization. Kuhlmann recommends the following proportions:—100 parts of ground sulphate of baryta, 40 coal, 170 saturated solution of manganous chloride, 13 chalk or lime; or 320–400 still-liquor, 100 barium sulphate, 30 to 35 coal (no lime). The MnS remaining behind on dissolving cannot be utilized; it yields too poor a gas for sulphuric acid-chambers when burnt.

The still-liquor has been mentioned in most processes for *recovering sulphur from soda waste, e. g.* by Townsend and Walker (patent, July 9, 1860), Mond (Sept. 8, 1868), Schaffner (Vol. II. p. 663), and P. W. Hofmann (Apr. 9 and Oct. 8, 1866).

The *free acid* of still-liquor has been proposed for an infinite number of objects:—*e. g.*, by Kuhlmann for absorbing the ammonia formed in the dry distillation of bones (patent, July 18, 1855); by T. A. Cook for purifying manganese itself from iron, earthy carbonates, &c. (patent, Nov. 1, 1856); for making $CO_2$ from carbonates many times; for extracting copper-ores by Haeffely, and by Deane (prov. prot. March 13, 1866; Chem. News, xiv. p. 287).

After neutralizing the free acid, Muspratt and Gerland (Dec. 9, 1856, and June 5, 1857) precipitate the iron by calcium carbonate, remove it by filtering, then precipitate the copper by $H_2S$, and, after the removal of the CuS, by calcium sulphide or soda waste the nickel, cobalt, and a portion of the manganese as sulphides; the MnS is extracted from the mixture by weak acid. Copper, cobalt, and nickel, which may also be precipitated together by calcium sulphide, are utilized in the ordinary manner; and the

manganous chloride remaining in the mother liquor may be employed for recovering $MnO_2$.

### *The Recovery of Manganese Peroxide from Still-liquor.*

This is of course by far the most important mode of utilizing still-liquor; and it has been aimed at by a great number of proposals, which will be briefly enumerated here, reserving only Weldon's, which has been entirely successful, for detailed description.

*By the Action of Atmospheric Air on Manganese Protoxide.*—This process, which has finally turned out the only available one, was, accidentally, also the first proposed for recovering $MnO_2$; Gossage prescribes (in a patent of Aug. 17, 1837) the precipitation of still-liquor with lime, running off the $CaCl_2$ liquor, and bringing the residue into violent contact with air. The next step was made by Binks and Macqueen (patent of May 19, 1860): they passed air, either cold or, preferably, heated to 200° or 300° C. and upwards, through water in which manganous oxide precipitated by lime was suspended. The peroxide formed in this way was to be agglomerated into lumps by pressing in the damp state or moistening with a hot saturated solution of $MnCl_2$ and drying. Weldon's first patent dates from July 26, 1866; the further steps will be explained in the next chapter.

Binks had already, on Feb. 8, 1839, patented the precipitation of MnO by alkalies and heating the precipitate in the air; but he lays the most stress on the subsequent treatment with nitrate of soda. Walters patented (March 24, 1843) heating manganese sulphate (obtained as residue on treating manganese-ore with equivalent quantities of sulphuric and hydrochloric acids), admitting "a small quantity" of air; "manganese" is obtained; and the $SO_2$ evolved may be converted into sulphuric acid. Glover (prov. prot. June 16, 1853) purposes to regenerate "black oxide of manganese" by heating manganous chloride in contact with air. Balmain (patent, March 31, 1855) precipitates the still-liquor by ammoniacal gas-liquor, obtains from the solution ammonium chloride, and from the precipitate, filtered on sand and heated to a red heat, manganese peroxide. It is advisable to mix lime with the wet sediment before igniting it. Haeffely, on July 3, 1858, patented exactly the same thing. Elliott (patent, Oct. 13, 1856)

proposes to decompose by heat the $MnCl_2$, purified from iron, into free HCl and a mixture of MnO and $MnO_2$, from which the former is dissolved out by weak acid. Pattinson (prov. prot. Oct. 21, 1856) precipitates MnO by lime, and exposes it to a carefully regulated heat below the melting-point of tin, in order to obtain $MnO_2$. Essentially the same thing was again patented by Hunter (June 1, 1860). On Aug. 11, 1866, Clark (for Cotelle) patented the heating of acid manganese-liquor in a reverberatory furnace; in the residue $MnO_2$ is said to remain. If HCl is admitted, the same $MnO_2$ is to decompose it continuously into chlorine and water [of course with the assistance of atmospheric oxygen].

Claus (No. 1054, April 8, 1867) patents the same process; he absorbs the weak chlorine by a shower of water holding hydrated lime or magnesia in suspension, and treats the hypochlorites formed with hydrochloric acid, to obtain strong chlorine.

Gorgeu (Compt. Rend. vol. lxxxviii. p. 769) states that by heating manganous nitrate and keeping it for a long time at a temperature of 155–162° a compound having the same composition as the mineral polianite is formed. Post (Berl. Ber. xii. p. 1459) could not confirm this.

The process of Jezler (Dingl. Journ. ccxv. p. 446) is only a modification of Weldon's process: it likewise aims at the manufacture of a calcium dimanganite, 2MnO,CaO, but as a dry powder. Pure $MnCl_2$ solution is to be precipitated with thick cream of lime; one half or a little more of the quantity required for precipitation is to be added, the precipitate separated from the liquor and spread out in the air. After drying it a little, it is exposed to a temperature of from 30° to 40° C. for some time, agitating it, and replacing the water evaporating. When the mass has become black by absorbing oxygen, it is deprived of most of the $CaCl_2$ by washing, and the oxidation finished by raising it to a higher temperature [how much?]; at the end the $CaCl_2$ can be completely washed out. If the first oxidation takes place when the mass is still liquid, a moment comes when the voluminous and flaky sediment becomes dense; and then the $CaCl_2$ can be easily removed. But the lime ought not to be removed by washing too soon; for only the proper proportion between Mn and Ca yields a high-strength dimanganite. The product is sometimes brown, sometimes black; it equals the best native manganese as regards the consumption of hydrochloric acid, gives off most chlorine even in

the cold; and the still requires only moderate heating towards the end. Powdery recovered manganese can be formed into lumps which will be firm after drying, by adding a small percentage of the semi-oxidized mass which was not heated and contains calcium chloride.

A proposal patented by Valentin (July 13, 1870) has but very little prospect of realization. Potassium ferricyanide is to serve as carrier of oxygen to precipitated MnO in the form of mud; the ferrocyanide formed is to be reoxidized into ferricyanide by a current of air, and in this way a continuous action exercised similar to that of nitrous acid in the manufacture of sulphuric acid. Less than 0·5 per cent. ferricyanide upon the weight of the manganese is to suffice for regenerating the latter; but the high price of that salt would make this loss quite sensible; and it could not be left in the manganese mud, because in that case very poisonous cyanogen compounds would be formed along with chlorine. Washing out the ferricyanide would entail the filtering and treatment of a very large bulk of mud, and could not possibly pay the expense.

*Utilization of Still-liquor by converting the Manganese into Permanganate.*—De Sussex and Arrott (patent, Aug. 29, 1844) precipitate MnO from the liquors, and ignite it in a reverberatory furnace with potash or soda in the state of hydrate or carbonate; the fused mass is dissolved, and from the liquor $MnO_2$ precipitated by the $CO_2$ of the air, or by $CO_2$ prepared for the purpose.

*Treating the lower Oxides of Manganese with weak Acid* for washing out MnO, whilst the $MnO_2$ remains behind.—This is one of the many proposals, mostly somewhat obscure, in Binks's patent of 1839. De Sussex and Arrott, according to their patent just mentioned, dry down the still-liquor, heat the residue with lime or magnesia, and treat the oxide thus obtained with weak muriatic acid to dissolve MnO; they also do this with natural low-strength manganese-ore. Elliott and Pattinson, on April 25, 1856, obtained provisional protection for exactly the same thing.

*Igniting with Nitrate of Soda.*—Binks (1839) heats dried-down still-liquor, or lower oxides of manganese prepared in any way, with nitrate of soda to a dark red heat in a retort; lime or chalk may also be added. This mixture is 1 part nitrate of soda, 2 dry "sulphate residue" (*i. e.* residue from evolving chlorine by sulphuric acid, common salt, and manganese), and 3 parts of the lower

manganese oxides or carbonates, obtained by his process—or else 1 part nitrate, 8 parts dry "sulphate residue," and 3 parts calcium hydrate or carbonate. The residue on being washed furnishes $MnO_2$; the NO escaping is to be brought into contact with a further quantity of the lower oxides or carbonate of magnesia in a moist state. The latter part of this proposal is repeated in the patent of De Sussex and Arrott (1844). Gatty patented (Aug. 22, 1857) essentially the same thing as Binks. $MnCl_2$ or $MnSO_4$ is to be mixed with its equivalent of sodium nitrate, the mixture dried and heated to a dark red heat in an iron retort. "Black oxide of manganese" remains behind, along with sodium sulphate or chloride, which is separated by lixiviation; the escaping nitrous gases are to be utilized for the manufacture of sulphuric acid.

This process was again taken up by Kuhlmann (Compt. Rend. lv. p. 247), who, however, converts the nitre-gas by air and water into nitric acid. In this way, from 100 $NaNO_3$ 125 or 126 nitric acid of sp. gr. 1·320 are said to be obtained, *i. e.* not much less than in the ordinary manufacture of nitric acid. According to Péan de St. Gilles (Rép. Chim. appl. 1862, p. 338) the decomposition commences at 220° C., and lasts for 8 or 10 hours. The residue is not $MnO_2$, but an oxychloride of the formula $3Mn_2O_3,MnCl_2$, which is very unsuitable for chlorine-making. A further application of the nitrous vapours proposed by Kuhlmann was, passing them over $Mn(OH)_2$, whieh is thereby converted into $MnO_2$. Kuhlmann asserts (Beilstein, Chem. Grossindustrie, 1873, p. 42) that in this case manganous nitrate is re-formed, which on being heated to 200° leaves $MnO_2$ behind and gives off all the nitrogen as available nitrous vapours, not as NO or N; thus the atmospheric oxygen might be transferred upon MnO *ad infinitum*. Kuhlmann patented this process for England on March 8, 1873. He precipitates the still-liquor with only one equivalent of lime, and consequently asserts that he gets an 88-per-cent. peroxide [?], whilst Weldon's process (infinitely more simple!) only yields 70-per-cent. peroxide. Another proposal of the patent is, draining the $Mn(OH)_2$ on coarse matting and employing it for Bessemer-steel making. The latter proposal seems to betray small confidence in the former. The way in which Rosenstiehl employed the same reaction in connexion with Hoffmann's sulphur-recovery process, has been described in Vol. II. p. 688, where it has also been remarked that this process is no longer carried out.

*Heating of Manganese Carbonate.*—This process was patented by Dunlop on May 31st and Nov. 22nd, 1855, and is still practised at St. Rollox. The same process was also patented by Gossage on Aug. 30, 1855, but too late. An improvement by Clemm (Dingl. Journ. clxxiii. p. 128), viz. employing magnesium carbonate in lieu of calcium carbonate in this process, and regenerating HCl by heating the magnesium chloride, has not been practically realized. Neither has this been the case with the proposal of Binks and Macqueen (patent, May 19, 1860) for passing hot air through $MgCO_3$ suspended in water. It appears that the reaction upon which Dunlop's patent and other similar proposals are founded, was discovered by Forchhammer; it has been especially investigated by Reissig for a large number of temperatures and different durations of the heating process (Ann. Chem. Pharm. ciii. p. 27). He found a temperature of 300° and three hours' action most favourable; the product then contained 73 per cent. $MnO_2$, and corresponded to the formula $2MnO_2,MnO$. [This would square exactly with Weldon's theory, that in his recovery-process the reaction stops at the formation of an "acid manganite."]

Dunlop's process is as follows. The acid still-liquor is first neutralized with ground chalk in open agitating-apparatus; the iron is also precipitated as hydroxide, but no manganese. The neutral liquor is pumped into very large, horizontal, cylindrical, wrought-iron boilers, about 10 feet in diameter and 80 feet long, fitted with a horizontal agitating-shaft. Here the liquor is mixed with the requisite quantity of ground chalk (excess of which is to be carefully avoided); the boiler is tightly closed, and by blowing in steam the pressure raised to 2 or 2½ atmospheres. By means of the pressure, the heat, and the agitation, complete decomposition is effected in 24 hours, producing a solution of $CaCl_2$ and a white precipitate of $MnCO_3$, while under ordinary circumstances this reaction does not take place. The contents of the boiler are forced by steam-pressure into settling-tanks; the $CaCl_2$ liquor is run off, the precipitate well washed, pressed, and partially dried on iron plates. It is now put into shallow iron bogies running on wheels, and introduced into a peculiar kind of oven divided by arches into four tiers one above the other, each of which holds twelve of those bogies; inside there are rails, upon which the bogies run with ease. The oven is heated from without, so that its temperature reaches 315° C.; it is hottest at the bottom. A current of air

enters at the lowest tier and passes through all four. Each fresh bogie is introduced at one end of the top tier, where it meets the coolest temperature and an atmosphere rather poor in oxygen; the bogies are gradually moved onwards, that at the end of each tier getting into the next lower tier; and they thus constantly meet a warmer air, richer in oxygen, which assists the conversion of the moist manganese carbonate into peroxide. The moisture must be renewed by frequent squirting of water. As a fresh bogie is put in once an hour, and the others must all be moved onwards accordingly, each of them remains in the oven for 24 hours. When they come out, their contents test 72 per cent. $MnO_2$; the remaining 28 per cent. are lower oxides of manganese and about 2 per cent. calcium carbonate. The thick paste is worked up for chlorine by HCl as usual, and is much more easily dissolved than native manganese. The plant required for this process is extremely costly, and has never been put up for the whole of the still-liquor even at St. Rollox. Outside of those works (where it is still in action) the process seems to have been tried only at Thann (Wagner's Jahresb. 1858, p. 122; Hoffmann, Report by the Juries, 1862, p. 37); but it was there given up after a short time, as the expense of fuel made it unremunerative.

# CHAPTER VI.

## THE WELDON CHLORINE-PROCESS.

ALL the numerous proposals for recovering the manganese, or for manufacturing chlorine without manganese, have issued in failure, with only three exceptions, viz. the processes of Dunlop, Weldon, and Deacon. In all other cases either the recovery of $MnO_2$ costs more than fresh manganese-ore, or the chlorine obtained is too dilute, or for some other reason the process does not pay. Of the three processes just mentioned we need not recur to Dunlop's, although up to this day 5000 tons of bleaching-powder per annum are made by it, because, for the reasons given before, this process has not extended beyond the St.-Rollox works, where it originated; the same firm, at their new works at Hebburn-on-Tyne, has introduced Weldon process, and not the Dunlop—which makes further comment unnecessary.

Practically the question is only as between Weldon's process and Deacon's. The former is worked with $MnO_2$, always regenerated by a current of air; in the latter the manganese oxides are not employed, but chlorine is procured by decomposing HCl and O (of the air) in contact with cupric sulphate. We shall first describe Weldon's process, and afterwards compare the relative position of the two.

The recovery of $MnO_2$ by the action of a current of air upon $Mn(OH)_2$ precipitated by lime has been repeatedly proposed (p. 192). Nearest to the mark came the process of Binks and Macqueen (1860); but they also did not succeed. It is the undoubted merit of Mr. Walter Weldon to have discovered the

right way. He also, as shown by his first patent of 1866, was not at first on the right track, but found it by persevering experiments when he had an opportunity of working out the process at the works of Messrs. Gamble and Co. at St. Helens.

Weldon's process is founded on the fact that freshly precipitated manganous hydroxide, suspended in a solution of calcium chloride, is, *in the presence of an excess of lime*, easily converted into peroxide by a current of air forced through the liquid. It is this *excess* of lime that has made the process successful. It had long been known that $Mn(OH)_2$ can be to a certain extent oxidized as it is precipitated from still-liquors by its equivalent of lime; but this oxidation remains so incomplete as to be useless in practice. Weldon found that manganous oxide treated in the wet way with air could at most be half-converted into peroxide, so that $Mn_2O_3$ is formed; but when a certain quantity of lime is added, the MnO under favourable circumstances can be completely converted into $MnO_2$, and that in less than one tenth of the time which is necessary for forming $Mn_2O_3$ in the absence of lime. This was the key to the splendid success which his process has had. But it should not be overlooked that Weldon has also worked out the technical details both of the plant and the process with great perseverance and care, so that nowadays the apparatus can be erected and started from his instruction without any difficulty. There is all the difference in the world between the crude and economically useless proposal of Binks and Macqueen, and the Weldon process, which now forms an integral part of the operations of well-nigh every larger alkali-works, both in England and on the Continent. This process is now almost more easily and safely carried out than any of the long-known operations in alkali-works. Weldon's merit has been fully recognized abroad by the bestowal upon him of the grand Lavoisier medal, and of a "Grand Prix" at the Paris exhibition of 1878. He must be said to have largely benefited chemical industry in general, and, by cheapening bleaching-compounds, also the bleach-trade and paper-making and the carrying-out of disinfection—that is, all mankind.

Weldon's manganese-recovery process is inseparably connected with his process of generating chlorine from the recovered peroxide. It is, on the whole, carried out everywhere according to the same principles and in very similar apparatus. The following description refers to an apparatus with which 6 tons of bleaching-powder

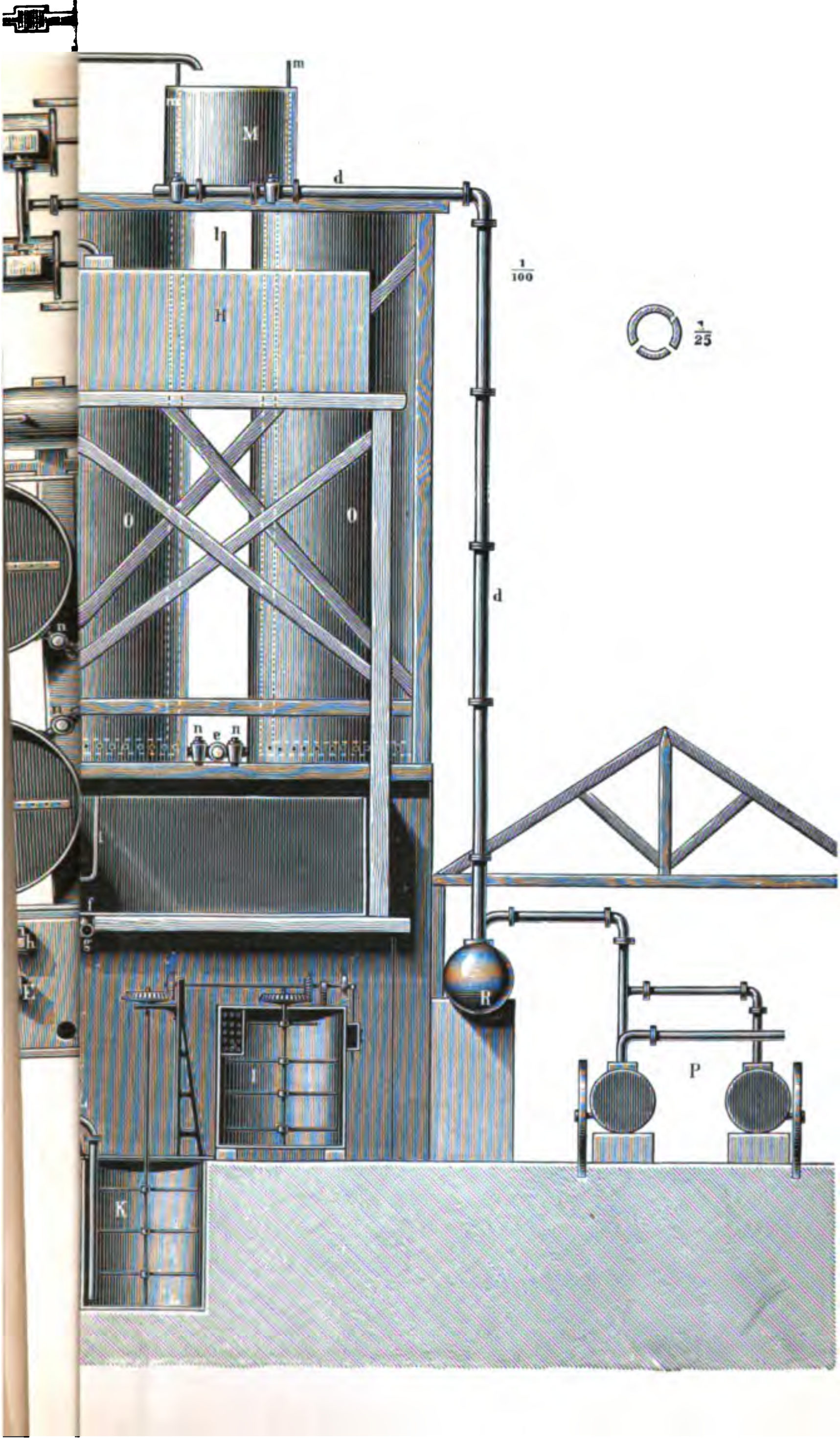
daily can be made by working single shifts, or 12 tons by day-and-night work; but in the latter case the stills should be larger, as they are afterwards represented in special drawings. Fig. 73 is a side elevation of the apparatus, fig. 74 a plan on the line A B of fig. 73, fig. 75 a section on the line C D of fig. 74.

E E are the mud-stills, which are here taken as 7 feet square and 10 feet high; their construction will be described in detail afterwards. T is an ordinary still, which serves for dissolving native manganese-ore, to make up for the loss in recovery, and which is so fixed that its waste liquor can be discharged directly into one of the mud-stills E. F is the neutralizing-well, which receives the manganese-liquor from E; this also will be described below. G is a pump, made of cast iron, with bronze piston, valves, etc.; it conveys the neutral manganese-liquor, free from iron, by the pipe *a* to the wrought-iron settlers H H. (These pumps, like all other apparatus belonging to this plant, are supplied by Messrs. Neill and Son, of Bold, near St. Helens.) They are worked by a special engine as double-acting force-pumps with a 6-inch barrel, and are built very substantially, so as to seldom require repair. Their valves are very easily accessible. Their suction- and delivery-pipes are 4 or 5 inches wide; the suction-pipe, so far as it dips into the manganese-liquor contained in the neutralizing-well, is sometimes made to turn on a swivel; it is then ordinarily protected from contact with the acid liquor, and need only be let down when the pump is to work. Failing this arrangement, there should be a few suction-pipes in reserve, as they are quickly corroded. There is a running-off cock attached to the delivery-pipe, by which the liquor standing in it is run back into the well. In order to make the pressure more uniform, and, as it were, to serve as an air-vessel, the upper end of the delivery-pipe *a* is continued 6 feet above the side branch conveying the liquor to the settlers.

*The chloride-of-manganese settlers* H H are made of $\frac{3}{8}$-inch boiler-plate, or of cast-iron flanged plates bolted together, with the usual strengthening stays. Wooden tanks caulked, or lined with lead, are very disadvantageous; the extra cost of the iron vessels is very quickly made up by saving the expense of the repairs and the long stoppages connected with the other kind of vessels. Well neutralized manganese-liquor does not act at all upon the iron. There must be at least two settlers, in one of which the liquor is left at rest while the other is being pumped into. Each of them is pro-

Fig. 75.

[*To face page* 200 (vol. iii.).



vided with a side discharge-pipe and sluice-valve *b* not far above the bottom; this is continued inside into a swivel pipe like that shown in figs. 237 and 238, in Vol. II. p. 557, or sometimes into a 4-inch indiarubber pipe, so that the liquor can be drawn off clear from the mud. The discharge-pipes unite outside in an iron pipe, which divides again into two branches, one for each oxidizer O O, provided with a sluice-valve each. These branch pipes enter the oxidizers at about two thirds of their height. The manganese-liquor is pumped alternately into one or the other settler. This is mostly done by separate valves for each; but a wooden or iron box *k*, with a plug-hole for each compartment, answers the same purpose. Each settler also has a large conical bottom-valve, worked by the handle *l*; by these the mud is removed from time to time. Below they discharge into large wooden or iron shoots (not shown), which convey the mud to a suitable place for further treatment.

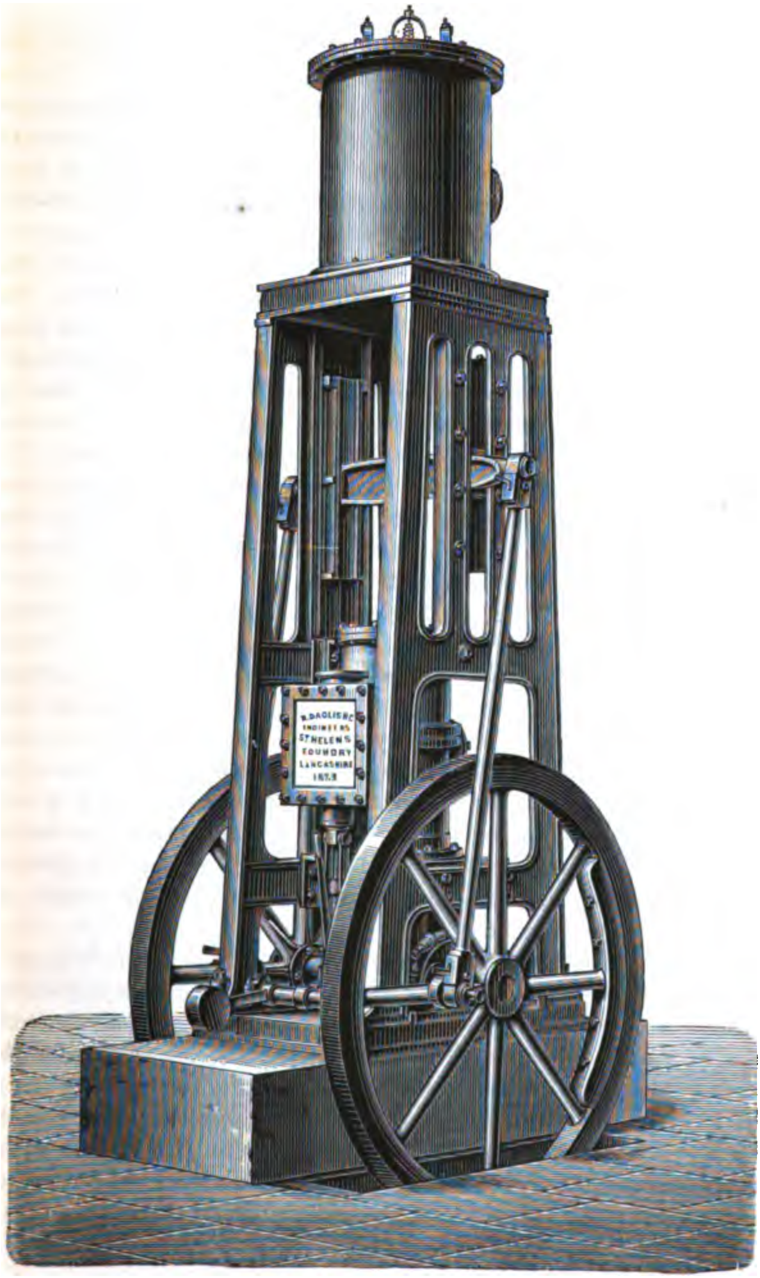
The settlers H H may be each about $18 \times 12 \times 6\frac{1}{2}$ feet, holding, when full, about 50 tons—making, along with their own weight, together about 104 tons. Consequently they must be very firmly mounted, especially as this has to be done at a great height above the ground. This is always effected by a wooden framework of 12 to 14-inch-square beams, resting upon the same foundation as the mud-settlers S S. This framework is represented in the drawing without the necessary staircases, gangways, etc.

In the *oxidizers* O O the recovery proper takes place. They are wrought-iron cylinders, $\frac{3}{8}$ inch thick (the upper third, which never contains liquid, but only froth, may be $\frac{1}{4}$ inch), open at the top, and with a flat bottom. They stand on a strong foundation, mostly of brickwork, upon which a wooden framework is erected for keeping the oxidizers in their places, and preventing them from shifting, notwithstanding the strong shaking on forcing the air through. The oxidizers are filled with settled manganese-liquor by the pipes *b b*, and are fed with milk of lime either directly by the pump L and the delivery-pipe *c*, or preferably from the iron tank M, into which the milk of lime is pumped first, and which discharges into either oxidizer by a separate valve *m m*; these are in the drawing shown only as plug valves; but they must actually be constructed in such a way that they can be regulated as well from the foot of the oxidizer. The upper lime-tank M must also be provided with an agitator; and since the application of machinery at that height occasions difficulties and expense for shaft-

ing, it seems advisable to fix a Körting's injector there, and agitate by a current of air. The unavoidable dilution by steam can do little harm during the short time this agitation goes on. Or else a small branch of the large blowing-pipe is put in to stir up the milk of lime. When this vessel M is not present, the oxidizers remain quite open; and in any case only a small portion is covered by bearers &c. The |7-inch pipe *d* conveys compressed air into the oxidizers; it comes from the air-vessel R, and sends a branch with valve to each oxidizer. This pipe, in spite of the greater expense and the loss by friction, must be carried to the top of the oxidizers and then descend to the bottom inside; otherwise the connecting flanges could not be kept right, owing to the shaking during the blowing. The same thing holds good of the milk-of-lime pipe and the steam-pipe; but as a fixed connexion cannot be dispensed with in the case of the manganese-liquor pipe *b*, the author found it suitable to interpose in this pipe, between the oxidizers and settlers, an equally wide (4-inch) indiarubber pipe, which entirely prevents the movements in O O being felt in the settlers H H. The air-pipe *d* descends to the bottom of O, and there branches off in the form of a cross, or in some other way, so that the blast is divided into many jets. The branches are closed at the end, and are perforated with a number of 1-inch holes slanting downwards (fig. 75, *a*); thus the mud does not penetrate into them so easily. Each oxidizer has also a 2-inch steam-pipe (not shown), passing over its top down to the bottom and branching off there; the steam-valve is placed outside in a convenient position for the attendant, near a ½-inch test-cock, 5 feet above the bottom. These are generally in or close to a small laboratory (testing-cabin) built against the oxidizer, from which also the valves for the milk of lime are accessible, and which is connected with the engine-room for the blowing-engine by an open communication, or at least by a speaking-tube. The discharge-pipes *n n* (6 inches wide) start from the bottom of the oxidizers, each provided with a sluice-valve, and continue into a common pipe *c*, which sends out a branch with 4-inch valves over each mud-settler.

The *manganese mud-settlers* S S are built just like the liquor-settlers H H and of the same size; but there must be at least 3, better 4 of them, provided. Each is fitted with a 2-inch swivel pipe *i* for running off the calcium-chloride liquor; these communi-

Fig. 76.



cate on the outside with a common pipe or, better, an open spout, conveying the liquor to a catch-well. At the bottom there is a 4-inch pipe *f* with sluice-valve, joined to the main pipe *g*, from which each of the stills E is fed by a pipe and sluice-valve *h*.

*For producing the current of air* the following arrangements are made:—Two steam-boilers N N, of about 6 feet diameter and 30 feet long, supply the steam for the blowing-engine P and all other steam required in the process (for the oxidizers, milk-of-lime tanks, chlorine-stills, pumps, and agitators). In case of need, *e.g.* during cleansing or repairs, one boiler may work by itself; but then all the operations cannot be performed at one time. The blowing-engine P in this case is sketched as a horizontal twin-engine, with two steam-cylinders of 18 inches diameter, air-cylinders of 2 feet 2 inches diameter, and 2 feet stroke; one of the cylinders may work by itself in case of repairs, but not so well. All the valves of the air-cylinders are of india-rubber. This is the kind of blowing-engine built by Messrs. Neill and Son of Bold; others prefer the vertical engine, fig. 76, built by Messrs. R. Daglish and Co., of St. Helens, with a 20-inch steam-cylinder, 2-ft. 3-inch air-cylinder, 3 feet stroke, and an 8-foot fly-wheel. The blast passes from the engine first into a regulator or air-vessel R of any shape, and from this by the 7-inch pipe *d* to the oxidizers. To the air-vessels a pressure-gauge and a pipe for running off the water are fixed; the latter comes from the air-cylinders, which are lubricated by a continuous small jet of water.

The blowing-engines will have to make from 40 to 60 strokes per minute, according to the amount of work to be done. For each ton of bleaching-powder to be made, about 300,000 cubic feet of air or one hour's work of 40- to 45-horse power may be taken as necessary. The exhaust-steam should be utilized for heating up the feed, the milk of lime, &c.

The *milk of lime* is made in the two iron cylinders I and K, each about 6 feet high and 7 or 8 feet wide, which can be conveniently placed beneath the mud-settlers. I serves for slaking the lime and preparing the milk, K for storing the latter and also for the lime-pump L; it is sunk in the ground, so that the whole contents of I may run into L. Figures 77 and 78 show this arrangement on a large scale. A donkey-engine *a*, bolted to I, drives the agitators of both cylinders. In I there is a cage *b*, formed of perforated metal plates, for receiving the lime; it occupies a

Fig. 77.

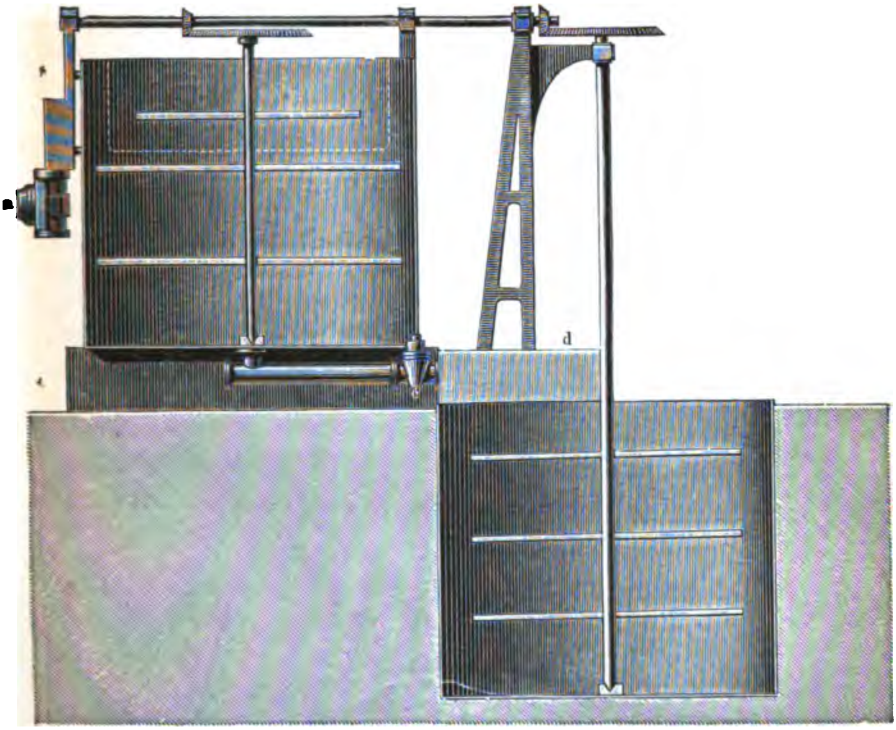
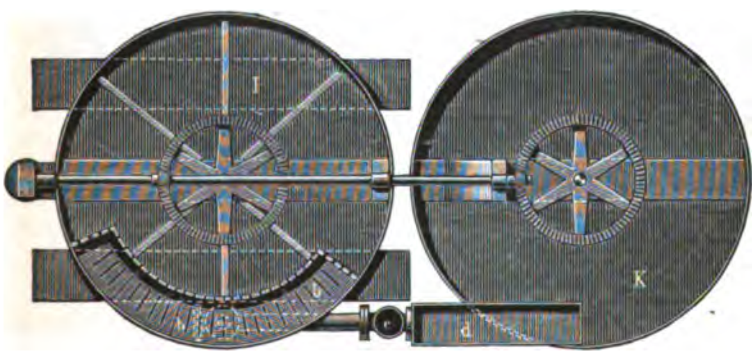



Fig. 78.

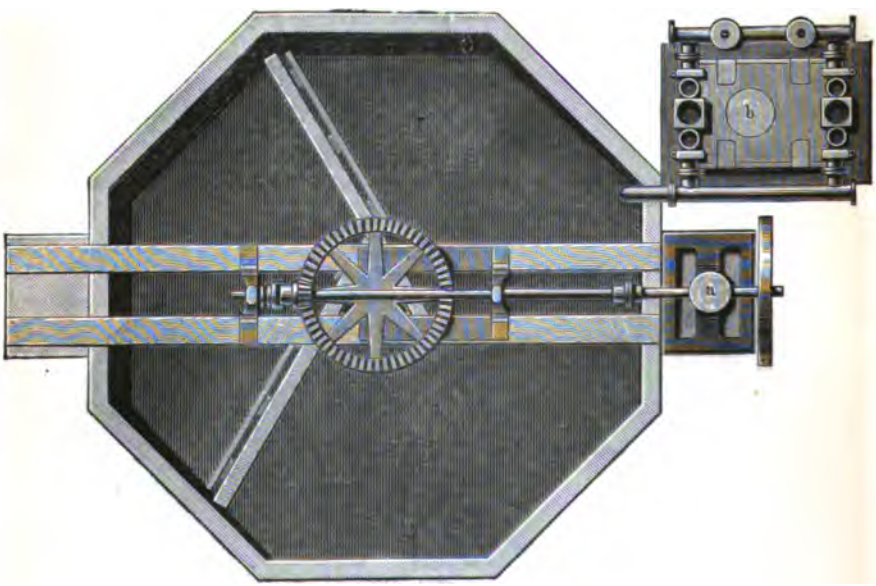



segment of an annular space in the upper third of I, one third or half round its circumference; the upper cross arm of the

agitator is accordingly shortened. The cock *c* runs the milk of lime from I through the finely perforated zinc plate in the sieve *d*, and from this into K.

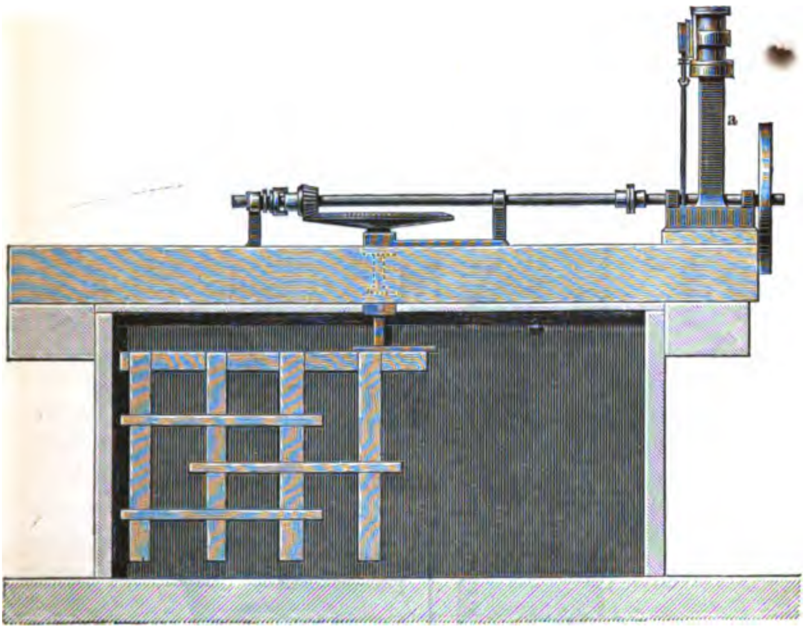
The *neutralizing-well* F (in figs. 74 and 75) is always sunk in the ground, and surrounded by a clay puddle in order to prevent the running-out of liquor as much as possible. It is either made of large stone slabs, in an octagonal shape, or of fire-bricks or hewn freestone, in a circular form. Of course the stone must be acid-proof and set in tar-pitch and sand in the most careful manner. At least once a week the well must be left filled for a night and exactly gauged, to control its being tight. A leak once formed, even if discovered, is very difficult to stop effectually. The well is covered with strong tarred planks, in which a large man-hole, a stoneware pipe for carrying the gas into the nearest chimney-flue, and a central aperture for the agitator are made. The latter is either suspended as in figs. 79 and 80 (where *a* is the

Fig. 79.




steam-engine for driving the agitator, *b* the pumping-engine for the manganese-liquor), the agitator itself being made of wood and fastened in an iron upper part, or it is made more substantially

Fig. 80.




with an iron shaft rotating in a footstep, as in fig. 75. The latter does not easily give out, in spite of the mud lying at the bottom, and is not so frequently out of repair as the former. There are in large works several of these wells; but one suffices for the apparatus here represented, 5 feet 6 inches deep and 13 to 15 feet wide.

The *chlorine-stills* employed in the Weldon process widely differ in shape from those used in the ordinary process. They are always composed of stone flags, and are much larger, especially much higher, than the stills for manganese-ore; they have no grating. The shape usual at small works (turning out 7 or 8 tons of bleach daily) is shown in figs. 81 and 82. Fig. 81 is a view from above, with a portion of the cover taken away; fig. 82 is partly a front and partly a sectional elevation. Upon a bottom-stone about 8 feet 6 inches square and 10 to 12 inches thick the four sides are erected in two tiers, one above the other. Fig. 83 shows the way in which the corners are joined together. Of course there is always a channel provided for the tar and china-clay cement ("black stuff"). The four sides are tied together by strong cast-

Fig. 81.

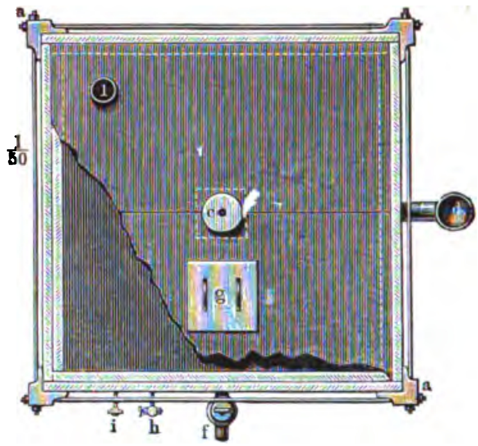
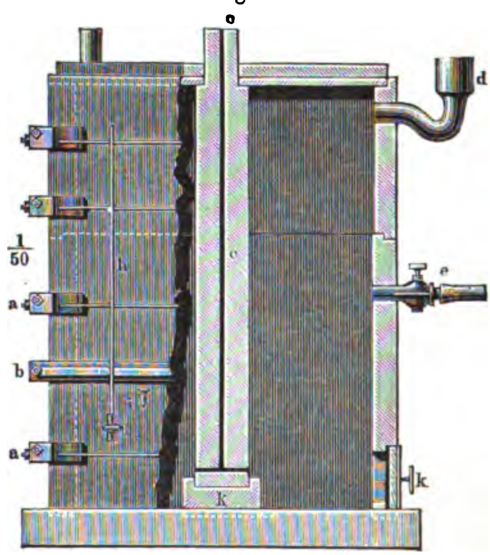



Fig. 82.




iron corner-brackets with screw-bolts passing through them, shown at *a a*; there are at least two sets of these for each tier. All iron work is thickly coated with coal-tar pitch; the corner-brackets do not touch the stone directly, but a piece of sheet lead is put in between; the screw-bolts are surrounded with indiarubber or

earthenware pipes at any place where they might be damaged by drops of acid. As the stills are exposed to pretty strong shaking during the steaming, and the joints may thus be loosened or even the stones be cracked, it is very useful to strengthen the lower tier in the way represented by bracing it with strong railway-plates pressing against the stones, a piece of sheet lead lying between; in the corners they are bent round in the way seen in fig. 83, and brought together by strong bolts. The steam-pipe *c* is made from a 16-inch-square stone column by drilling into it a central 1½-inch hole, and close to the bottom three or four cross holes. At the bottom it rests in a stone socket *k*; at the top it is joined to a lead steam-pipe, continued into an iron one, the cock of which should be protected in the way described on p. 142. Instead of a stone column, at some works strong earthenware pipes of about 6 inches diameter and 1½ inch bore are employed; but these must be made in two pieces, as such long pipes (13 feet) cannot be made in one; and the joint is very difficult to keep tight. On the top the square steam-column is dressed in a circular shape, affording a support for the two halves of the top cover, which also rest in recesses of the side stones. The manganese mud is run in by a 6-inch-wide lead or stoneware funnel with swan-neck pipe, above which is arranged the sluice-valve of one of the branches of the mud-pipe from the mud-settlers. Several other hydraulic lutes are employed for the same purpose, often fixed on the cover itself as that shown in fig 84. *e* (fig. 82) is the 3-inch stoneware cock for feeding with acid; this may also be placed higher up, but not lower than one third of the height of the still from the bottom. This cock is kept tight against the stone by a contrivance shown

Fig. 83.

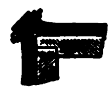


Fig. 84.

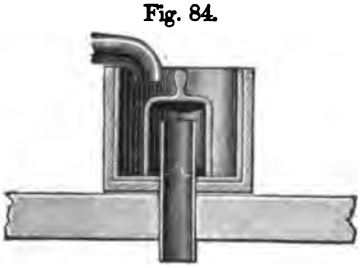
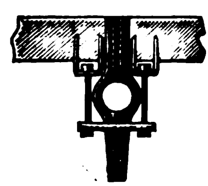


Fig. 85.



on an enlarged scale in fig. 85. The cock should not be cemented

into the acid-pipes outside, but connected with them by an india-rubber pipe, as otherwise the shaking of the still easily loosens the joints of the pipes. A similar cock is fixed close above the bottom for discharging the manganese-liquor at the end of the operation, unless it is preferred to employ a stoneware pipe continued into a 4-inch indiarubber pipe squeezed together by an iron clamp. Some manufacturers prefer this latter arrangement on account of the liability of earthenware cocks to break; but neither do the indiarubber pipes last long, and their renewal costs much more than that of the earthenware cocks. *g* is the lid of a man-hole for occasionally entering the still; another man-hole is made close above the bottom, and is closed by a wooden lid covered with a sheet of india-rubber, pressed against a recess of the stone by a screw-bolt arrangement. Neither man-hole need be opened frequently, as the still but rarely requires cleaning. There is also a stoneware pipe with outlet-cock for putting-in the glass liquor-gauge pipe *h* (which is kept tight in it by a bit of indiarubber tubing), also a small testing-cock, *i*, and a gas-pipe, *l*, on the top. That the stills should be erected on a most substantial foundation, hardly requires mentioning.

For large works the square shape of still is not so well adapted as the octagonal; for it is important, in regard to simplifying and superintending the work, to employ only a few stills, and consequently make them of much larger dimensions than those here stated; and this cannot very well be done with square stills, as stones of sufficient size would not be easily procurable. Such an octagonal still is represented in figs. 86 and 87, on a scale of 1 to 50; but at some works they are made even much larger, up to 12 feet wide and high. Fig. 86 is a view from the top, with part of the cover removed; fig. 87, a sectional elevation, omitting the ironwork. The bottoms in this case cannot be made of a single stone; they must be composed of two or four stones, bound together by corner-brackets and bolts, *a a*. The octagonal sides, also in two tiers, are joined at the corners by indiarubber cord, lying in shallow grooves of the adjoining faces (comp. the description, Vol. II. p. 198). Or else indiarubber bands with raised edges, like ●———●, are employed, and corresponding grooves made in the stones. The stones are bound together by the brackets *b b* and screw-bolts; sometimes by strong cable-chains, drawn up tight by coupling-screws. These do not press immediately upon the side-

Fig. 86.

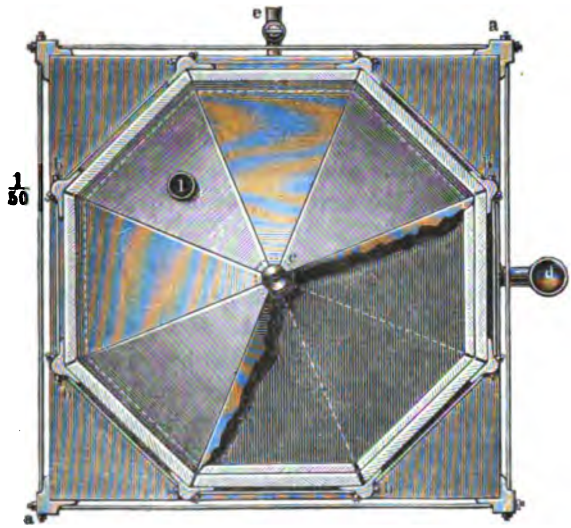
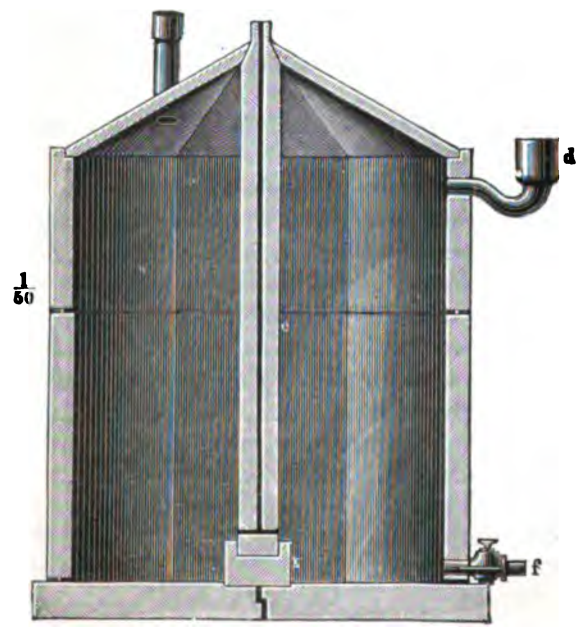



Fig. 87.



stones, but on strong wooden posts, of which two are present for each of the eight sides, and from which the chains are at the same time suspended on pegs; perfect tension is secured by means of wedges. The top-cover is usually made dome-shaped; eight triangular stones rest with their bases in recesses of the side stones; and their apices lean against the head of the stone steam-column *c*, shaped to suit this. The other parts represented here, and noted by the same letters as the similar parts of the square stills, require no explanation.

The following amount actually spent in 1873 upon *erecting plant* for Weldon's chlorine-process will give a good idea of the cost, although it should be remembered that the prices of iron-work, labour, &c. were then at their highest. The plant was intended for turning out 6 or 7 tons of bleaching-powder daily, and was sufficient for this purpose; but a second oxidizer would have been very useful for heating up a second charge of manganese-liquor while the first one was being blown. The engine was a single one, but sufficient for its purpose. The steam-boiler was too small, and had to be supplemented by steam from other boilers; so that this item should be doubled. The item for pipes &c. is very high, because the stills were about 50 yards distant from the oxidizers. The prices were increased by the necessity of procuring all materials and labour from the other end of England.

I. *Contract for engineering-work* (all supplied at the place and erected ready for starting):—

| | £ | s. | d. |
|---|---|---|---|
| One blowing-engine with 17½-inch steam-cylinder, 2-ft. 2-in. air-cylinder, and 2 ft. stroke ......... | £280 | 0 | 0 |
| One 7-inch sluice-valve for air .......................... | 4 | 10 | 6 |
| Pipes for distributing air and steam in the oxidizer... | 31 | 0 | 0 |
| Five 6-inch sluice-valves for running manganese mud into the settlers .................................... | 19 | 6 | 3 |
| Six 4-inch sluice-valves for running manganese mud out of the settlers .................................... | 15 | 9 | 0 |
| Two 4-inch sluice-valves for running manganese-liquor to the top settlers .................................... | 5 | 3 | 0 |
| Four 2-inch swivel-pipes for calcium chloride ......... | 4 | 12 | 0 |
| Two plug valves in the top settlers .................... | 2 | 6 | 0 |
| Carried forward ......... | £362 | 6 | 9 |

| | £ | s. | d. |
|---|---|---|---|
| Brought forward ......... | £362 | 6 | 9 |
| One 6-H.P. steam-engine, shafting, and agitator for the neutralizing-well .................................. | 115 | 10 | 0 |
| One 6-inch double-acting force-pump and engine, with bronze working-parts, for chloride of manganese | 83 | 10 | 0 |
| One 2-inch outlet-cock for delivery-pipe of the same. | 1 | 2 | 6 |
| One 6-inch double-acting force-pump and engine for milk of lime ........................................... | 78 | 10 | 0 |
| One 2-inch outlet-cock for delivery-pipe .............. | 1 | 2 | 6 |
| Two cylinders for slaking lime and storing milk of lime, 8 feet in diameter, 7 feet high, with cage for lime, strainer, agitator, and steam-engine ... | 168 | 0 | 0 |
| One oxidizer, 9 feet in diameter, 26 feet high ......... | 126 | 0 | 0 |
| Four manganese-mud settlers, at $16 \times 12 \times 6$ feet, in one piece, 16 tons weight at £21 ................. | 336 | 0 | 0 |
| One air-vessel for blast .................................. | 18 | 0 | 0 |
| Two air-vessels for pumps ............................... | 5 | 9 | 0 |
| Pipes—7-inch, 6-inch, and 4-inch ....................... | 90 | 10 | 0 |
| Erecting valves, pipes, &c. ................................ | 30 | 0 | 0 |
| | 1416 | 0 | 9 |
| II. *Other plant.* | | | |
| Settlers for chloride-of-manganese liquor.............. | 200 | 0 | 0 |
| Foundations and wood frame ............................. | 221 | 12 | 2 |
| Two large mud-stills $7 \times 7 \times 10$ feet inside ........... / Two ordinary native-manganese stills, shed, pipes, &c. | 374 | 7 | 5 |
| One neutralizing-well, 14 feet diameter................. (Agitator and engine, see above). | 75 | 10 | 10 |
| One steam-boiler with two fire-tubes, 7 feet diameter, 30 feet long, with mountings ........................ | 328 | 14 | 6 |
| Setting, erecting, and boiler-shed ....................... | 177 | 17 | 8 |
| Sundry small labour ...................................... | 41 | 14 | 11 |
| General work, drainage, excavating, &c. .............. | 41 | 6 | 4 |
| | £2877 | 4 | 7 |

We shall begin the description of the *work carried on in Weldon's chlorine-process* at the point where the acid still-liquor runs into the neutralizing-well, because in every case the process is commenced with such still-liquor, obtained from manganese in the

ordinary way. The liquor must be first *neutralized* by adding calcium carbonate till all free acid has been saturated, and all iron precipitated as hydroxide. For this purpose ground chalk, limestone, lime riddlings, &c. are employed; the more finely ground they are, the less excess of them is necessary, and the more quickly the work goes on. Since the mud left here is not merely worthless, but causes the principal loss of manganese by mechanical absorption, the smallest possible excess is desirable. Some factories employ milk of chalk made in a mortar-mill, by which the neutralization is accomplished at once, and without any excess to speak of.

In the neutralizing, together with much carbonic acid, the free chlorine, never absent in still-liquors, is given off; hence the well must be kept covered and connected with the chimney by a stoneware pipe. Too quick an addition of lime causes the liquor to froth over. The agitator must be constantly going round, and must be strongly built, as it suffers considerably. The process is finished when a sample of the liquor, poured on ground chalk, causes no effervescence.

For neutralizing still-liquor from native manganese very much limestone is required, up to four times the weight of the peroxide formed. This is avoided if the liquors from the native-manganese-stills are first run through the Weldon mud-stills, in which case its free HCl is usefully employed. With liquor from recovered peroxide 10 to 30 parts of ground chalk or limestone are still required for 100 parts $MnO_2$, according to the degree of division.

The neutralized manganese-liquor, along with the mud, is pumped up to the liquor-settlers H H (figs. 73 to 75). It is most important that it should become perfectly clear by subsidence; any mud remaining in suspension not merely contaminates the recovered peroxide by gypsum (from the sulphuric acid contained in the muriatic acid), calcium carbonate, ferric oxide, &c., but also very frequently causes the contents of the oxidizer to froth over during the blowing. With muddy liquors low-strength manganese mud with a high "base" is always obtained.

Black (*loc. cit.*) gives the following analysis of waste mud; but the large quantity of calcium carbonate in excess there shown would certainly have been avoided by better grinding and more careful employment of the chalk.

| | From native manganese. | From recovered peroxide. |
|---|---|---|
| $CaSO_4$ | 0·68 | 0·46 |
| $CaCO_3$ | 35·64 | 55·15 |
| $MgCO_3$ | 0·29 | 0·75 |
| $CaCl_2$ | 6·06 | 5·71 |
| $MnCl_2$ | 2·41 | 1·38 |
| $Fe_2O_3$ | 1·83 | 1·86 |
| $Al_2O_3$ | 1·57 | 0·57 |
| $SiO_2$ | 1·17 | 2·10 |
| $H_2O$ &c. | 50·35 | 32·02 |
| | 100·00 | 100·00 |

The settling mostly takes but a few hours; the clear liquor is then run, by carefully lowering the inner swivel-pipe, into one of the oxidizers, where it is just required. The mud can be left in the settlers H H till it has accumulated too much—which of course will happen much sooner or later according to circumstances, often after only two or three batches. It is then run off by opening the plugs *l l*, first to some vessel (not shown in the drawing) where it is left to subside again in order to draw off the clear manganese-liquor as closely as possible; then it is often washed—but not too much, in order to avoid diluting the manganese-liquor. The best effect is produced by filter-presses, which make any dilution unnecessary. On the more or less careful way of treating this waste mud the loss of manganese in the whole recovery-process chiefly depends.

The author has proposed the following use for this waste mud—patented in 1877, but employed by him at least four years previously. It contains much ferric oxide and often even manganese peroxide, and is consequently eminently adapted for disinfecting the drainage from old tank-heaps. The way in which it can be employed for this purpose has been indicated in Vol. II. p. 637.

The chloride-of-manganese liquor must now be treated with *lime*. For this very pure lime (free from magnesia especially) is required, which should be burnt down to a maximum of 2 per cent. of carbonic acid, but should not be overheated so as not to be slaked easily and completely. The drawbacks connected with incomplete burning are self-evident; those of partially burning "dead" are, that the milk of lime, even after straining through fine wire gauze

etc., contains many minute grains of unslaked and consequently chemically inactive lime, which cannot assist the operation in the oxidizers, but remains behind as injurious "base," causing a waste of hydrochloric acid. The proper state of the milk of lime is soon known from its uniform appearance and the absence of gritty particles in it. The damage done by magnesia is very great. Whilst most of the lime during the operation is converted into calcium chloride and its solution is afterwards mostly removed by decantation, the whole of the magnesia remains in the manganese mud as part of that portion of the "base" which is not combined with $MnO_2$. Having been converted in the stills into $MgCl_2$, it goes back to the oxidizer in that state. So long as any $MnCl_2$ remains undecomposed, the $MgCl_2$ remains undecomposed also; but the first effect of the excess of lime is to reconvert the $MgCl_2$ into $MgO$, the quantity of which present is now increased by that arriving fresh with the lime. The magnesia thus continually accumulates, causing the mud to become continually more and more basic, and thereby causing the consumption both of acid and of lime, per unit of chlorine obtained, to increase with every repetition of the operation. This evil may be, to some extent, avoided by using more than the normal quantity of final liquor, since, with time, after the $MnCl_2$ of the final liquor has reacted on half the lime (see below) in the $CaOMnO_2$, it will react on any $MgO$ present before reacting on $CaO(MnO_2)_2$, converting the $MgO$ into $MgCl_2$, some of which will then be removed with the $CaCl_2$. This remedy, however, can at best be only partial, since only a portion of the $CaCl_2$ present with the mud, and therefore of any $MgCl_2$ mixed with it, is decanted each time; and it is, moreover, very expensive, owing to the reaction of $MnCl_2$ on $MgO$ requiring an excessive time. It involves the risk, too, of impatient workmen running the batches off before the excess of $MnCl_2$ has completely reacted, thereby occasioning excessive loss of manganese.

It is thus evident that those descriptions of lime which burn badly and contain over 1 per cent. magnesia or other impurities are not fit for the Weldon process. The lime intended for this purpose is not slaked in the ordinary way to a dry powder; it has been found that much better and more active milk of lime is produced by introducing the quicklime directly into hot water. This is done in a cylindrical vessel with agitator (comp. figs. 77 and 78, p. 205); a strainer, formed of perforated metal plates, is fixed in the upper

part of the vessel, into which the quicklime is put, and which retains stones and any other coarse impurities, while the circulating water washes out the finer particles. Before running into the storage-vessel, the milk of lime passes another strainer of finely perforated sheet zinc or wire gauze; in larger works this strainer is an inclined rotating cylinder, at the lower end of which the gritty particles are discharged, while the milk runs through the fine holes in the sides of the cylinder. The strained milk of lime ought to be as strong as possible, containing from 20 to 22½ lb. CaO per cubic foot.

Supposing that there is a stock of well-settled manganese-liquor and properly made milk of lime on hand, one of the oxidizers is half-filled with manganese-liquor, of which a larger quantity must be in reserve in one of the settlers H H. Under normal circumstances the manganese-liquor would be strong enough to correspond to about 3¾ lb. $MnO_2$ per cubic foot. It is heated by blowing in steam to 55° C., and milk of lime run in while the blast commences to work slowly. The milk of lime is contained in a gauged tank; and its initial level is exactly noted. When the point has been approached at which all manganese has been precipitated, constant testings are made; and the supply of lime is stopped as soon as that point has been reached. The testing is done by taking small samples of liquor (well mixed by the blast) from the small cock in the oxidizer in or near the testing-cabin (p. 202), filtering them, and trying the filtrate for alkaline reaction by red litmus-paper. This indicates very accurately any excess of lime, which is much more soluble in a solution of $CaCl_2$ than in pure water, at least at a temperature of 50° or 60° C. The filtrate is also tested with strong bleach-liquor, by which no brown colour (from $MnO_2$) must be produced. In many factories the milk of lime is pumped directly from the vessel K (fig. 78), which is provided with a liquor-gauge, into the oxidizer. In this case the pumping must cease directly the point of neutrality has been reached; the level of the milk of lime in K is read off, and the third or fourth, etc., still needed (see below) is pumped in. It is much safer and more convenient to pump the milk of lime at once into the tank M, fixed above the oxidizers, or at least at the height of the settlers H H; from this the milk of lime, by means of a valve accessible from below, is run slowly or quickly, as it may be required, into the oxidizer, and that by the man in the testing-cabin, who is thus independent of the

man at the pump. In any case the number of measures of milk of lime used is read off, and a quarter or a third of the quantity used is run in in excess. Evidently any error exceeding the point of precipitation in the first addition must cause three or four times as much error in the second addition. Some works only add one fifth. This depends on the nature of the lime, the strength of the liquors, and other circumstances not quite explained; but under like conditions the same excess is always required, as is proved by the quantity of "final liquor" used at a later stage. When working with liquors from native manganese, *i. e.* starting the process from the first, the second addition of lime should not be made all at once, but in several portions at intervals of a quarter of an hour, lest a "stiff batch" be produced. As soon as the second addition of lime has been made, *i. e.* as quickly as possible after precipitating the manganese as MnO, the blast is put on with full strength and kept at this; otherwise a "stiff batch" would be produced, as inversely a "red batch" is formed when the blast is put on fully before the lime has been put on. We shall come back to these phenomena again.

At this stage the contents of the oxidizer consist of a mixture of hydrated manganese protoxide and free calcium hydrate, the former suspended, and the latter partly suspended and partly dissolved, in solution of calcium chloride. The chief reason why an excess of lime is added is the fact, discovered by Weldon, that when manganese hydroxide is treated by atmospheric air in presence of a soluble base, very much more of it is converted into $MnO_2$, and that in very much less time, than when manganese hydroxide alone is so treated. At the temperature actually employed in the Weldon oxidizer, in the absence of any base other than itself, only one third of the $Mn(OH)_2$ would become peroxidized, the product being red oxide, or $Mn_3O_4$; if the operation were performed at the temperature of the atmosphere, and the treatment with air continued sufficiently long, one half of the $Mn(OH)_2$ would become converted into $MnO_2$, but not more than half, however long the treatment with air might be continued. The product of the treatment of $Mn(OH)_2$, alone by air in the wet way is thus always a "manganite of manganese"—either $Mn_3O_4$, consisting of one of $MnO_2$ combined with two of MnO, or $Mn_2O_3$, consisting of one of $MnO_2$ combined with one of MnO, according to the temperature at which the operation is performed. The fact that the whole of

the $Mn(OH)_2$ can be converted into $MnO_2$ if a full equivalent of lime be present, Weldon explains as being due to CaO replacing, and so permitting to become peroxidized, the MnO which would otherwise become locked up in combination with $MnO_2$.

The principal advantage of this replacement of MnO by CaO consists in the fact, already referred to, that to obtain a given quantity of $MnO_2$ in the state of calcium manganites requires less than a tenth of the time, and consequently less than a tenth of the coal and less than a tenth of the apparatus, which would be required to obtain the same quantity of $MnO_2$ as $Mn_2O_3$. While $MnO_2$, recovered from still-liquors in the state of calcium manganites, is very much less costly than native manganese, $MnO_2$ similarly recovered as $Mn_2O_3$ would thus be very much more costly than native manganese. But this substitution of CaO for MnO has a further advantage. While the richest product which can be obtained by treating $Mn(OH)_2$ alone by air in the wet way is $Mn_2O_3$, containing a full equivalent of combined "base," and so consuming 6 HCl per 2 Cl liberated by it

$$(Mn_2O_3 + 6\,HCl = 2\,MnCl_2 + 3\,H_2O + 2Cl),$$

a portion at any rate of the Weldon product consists of an "acid manganite," $CaO(MnO_2)_2$, or $CaMn_2O_5$, which consumes one sixth less acid than $Mn_2O_3$ consumes, giving 4 Cl for 10 HCl:

$$CaO(MnO_2)_2 + 10\,HCl = CaCl_2 + 2\,MnCl_2 + 5\,H_2O + 4\,Cl.$$

The proportion of this acid manganite is sometimes sufficient to reduce the "base" in the Weldon product to 0·6 of an equivalent per 1·0 equivalent of $MnO_2$; but the combined base, together with the basic bodies not combined with $MnO_2$, but present as accidental impurities, more usually amounts to 0·7. With 0·7 of base, however, the Weldon product consumes only 5·4 HCl for each 6 HCl which would be required by $Mn_2O_3$; while its regeneration moreover requires only 1·7 CaO per 1·0 of $MnO_2$ in it, instead of the 2·0 CaO which would be required for the production from $2\,MnCl_2$ of 1·0 of $MnO_2$ as $Mn_2O_3$.

A consumption of 5·4 HCl per 2 Cl is much greater than that calculated for pure $MnO_2$. But manganese peroxide very rarely occurs in nature free from lower manganese oxides and other matters absorbing acid, especially ferric oxide; and such pure ore is not at all accessible to the bleaching-powder-maker, owing to

its high price. Actually, in the *best* case as much acid is required with native manganese as with the regenerated peroxide, and nearly always much more with the former, because incomparably more free acid must be left in the still-liquors than when the thin mud of recovered peroxides is made use of.

The "manganites" always cited in the Weldon process have certainly never been examined in a pure and absolute state; they are in any case amorphous compounds, always mixed with impurities. But there are some good reasons for assuming that such compounds do exist; for it has been noticed that, in the action of $MnCl_2$ in excess upon the compound $CaO,MnO_2$ (or a mixture equivalent to this in composition, one of which must be formed in the Weldon process), one half of the CaO acts differently from the other half. Two reactions in fact take place, one instantaneously, the other requiring much time. The first gives acid calcium manganite and free $Mn(OH)_2$:

$$2CaO,MnO_2 + MnCl_2 + 2H_2O = CaH_2(MnO_3)_2 + CaCl_2 + Mn(OH)_2.$$

The other gives no free $Mn(OH)_2$, but simply converts $CaH_2(MnO_3)_2$ into the corresponding manganite of manganese:

$$CaH_2(MnO_3)_2 + MnCl_2 = CaCl_2 + MnH_2(MnO_3)_2.$$

That $MnO_2$ has distinctly acid properties, has been clearly proved by a number of chemists during the last few years from independent reasons. Only Post (Ber. d. deutsch. chem. Gesellsch. xii. p. 1454) denies the existence of "calcium manganite;" but his analytical methods are open to exception, and he cannot at all be considered to have proved his case. Neither does a further paper of his (*ib.* p. 1537) contribute materially to the elucidation of the Weldon process; and the discussion carried on between Post and the Author, first in 'Dingler's Journal' (1879), then in the 'Chemieal News' (1880), seems to have left the matter where it stood before. Very important in this respect is a paper read by Mr. Weldon before the Newcastle Chemical Society in 1880 (Chemical News, vol. 42).

Some weighty reasons have been adduced by Volhard (Annalen der Chem. u. Pharm. cxcviii. p. 354) for the assumption that manganese dioxide is in reality manganous manganate or permanganate. If that were the case, Weldon's "manganites" would become basic salts of manganic acid. But as the matter is so uncertain,

and the elucidation of the Weldon process is very much assisted by the assumption of the acid functions of $MnO_2$ itself, we shall, for the sake of convenience, continue to use the theory of manganous acid and of manganates, as held by Weldon.

While, by using a full equivalent of excess of lime in the Weldon process, the whole of the $Mn(OH)_2$, or the whole of it within 1 or 2 per cent., can be converted into $MnO_2$, a full equivalent of excess of lime is never now used in practice. The use of so large an excess would be too apt to give "stiff batches" (see below), and would have no corresponding advantage. It would yield a product consisting almost entirely of $CaOMnO_2$, and so containing a full equivalent of combined base; and although this might be reduced to 0·7 by acting on one half of the lime in that compound by $MnCl_2$, and oxidizing the resulting free $Mn(OH)_2$, the quantity of final $MnCl_2$ required would be inconveniently large. It is found better to use only from 0·6 to 0·7 of excess of lime; and in the best-managed works the porportion of excess used is never less than 0·6 or greater than 0·7, whether the nominal excess be one half, as in works where the lime is of such quality that the manganese is all precipitated by about 1·1 eq. CaO, or whether it be only one fifth, as in works using a quality of lime acting so much less readily that 1·3 to 1·4 eq. has to be added before the manganese is completely precipitated. With 0·6 eq. of excess of lime, the degree of oxidation obtained is usually about 86 per cent., the product, before the final liquor, consisting, in Weldon's view, of:—

$$\left.\begin{array}{l}0{\cdot}14\ MnO_2\\ 0{\cdot}14\ MnO\end{array}\right\}\text{ as } Mn_2O_3\text{, or } MnOMnO_2.$$

$$\left.\begin{array}{l}0{\cdot}48\ MnO_2\\ 0{\cdot}48\ CaO\end{array}\right\}\text{ as } CaMnO_3\text{, or } CaOMnO_2.$$

$$\left.\begin{array}{l}0{\cdot}24\ MnO_2\\ 0{\cdot}12\ CaO\end{array}\right\}\text{ as } CaMn_2O_5\text{, or } CaO(MnO_2)_2.$$

Such a product contains $0{\cdot}14+0{\cdot}48+0{\cdot}12=0{\cdot}74$ total protoxides per $0{\cdot}14+0{\cdot}48+0{\cdot}24=0{\cdot}86$ $MnO_2$, or 0·86 eq. "base" per eq. of $MnO_2$. If $MnCl_2$ be added to it until the filtrate from a sample gives a manganese reaction, it will decompose 0·24 eq. $MnCl_2$, being the quantity corresponding to one half the lime in its 0·48 of CaOMnO. If the treatment by air be then continued until

absorption of oxygen ceases, the 0·24 of further $Mn(OH)_2$ so obtained will become $Mn_3O_4$, or $Mn_2O_3$, according to temperature. If it becomes $Mn_3O_4$, the final product will consist of:—

$$\left.\begin{array}{l}0{\cdot}14\ MnO_2\\0{\cdot}14\ MnO\end{array}\right\}\text{ as } Mn_2O_3.$$

$$\left.\begin{array}{l}0{\cdot}08\ MnO_2\\0{\cdot}16\ MnO\end{array}\right\}\text{ as } Mn_3O_4.$$

$$\left.\begin{array}{l}0{\cdot}72\ MnO_2\\0{\cdot}36\ CaO\end{array}\right\}\text{ as } CaO(MnO_2)_2.$$

If the $Mn(OH)_2$ becomes $Mn_2O_3$, the final product will consist of:—

$$\left.\begin{array}{l}0{\cdot}26\ MnO_2\\0{\cdot}26\ MnO\end{array}\right\}\text{ as } Mn_2O_3.$$

$$\left.\begin{array}{l}0{\cdot}72\ MnO_2\\0{\cdot}36\ CaO\end{array}\right\}\text{ as } CaO(MnO_2)_2.$$

The base in the former case will be 0·14+0·16+0·36=0·66 per 0·14+0·08+0·72=0·94 $MnO_2$, or 0·7 eq. per eq. $MnO_2$, while the average degree of oxidation will have been reduced from 86 per cent. before final liquor to 75·8 per cent. at the end of the operation. In the latter case, the final base will be 0 26+0·36=0·62 per 0·26+0·72=0·98 $MnO_2$, or 0·632 per eq. $MnO_2$, and the average degree of oxidation at the end will be 79 per cent.

The proportions of base here spoken of refer only to the *combined* base. There are always present, however, as impurities, basic bodies not combined with $MnO_2$, and especially small quantities of MgO and $CaCO_3$. The total "base," as shown by the ordinary methods of testing Weldon mud, includes these impurities. These impurities should never be present in sufficient quantity to raise the total base above 0·7.

The quantity of lime which must be run into the oxidizer, before a filtered sample ceases to give the manganese-reaction with bleaching-powder, differs according to circumstances, but always exceeds the exact equivalent of the manganese present. Freshly precipitated $Mn(OH)_2$ is soluble to a sensible extent in a neutral solution of calcium chloride, and is indicated by bleaching-powder and other reagents. Hence the reaction with bleach-liquor only ceases when

a certain amount of lime over and above the equivalent has been added, and thus oxychloride has been formed. Moreover all the molecules of CaO in the milk of lime do not take part in the reaction upon manganous chloride; there are always coarser particles present, which, during the few minutes occupied by the precipitating process, have no time to act upon $MnCl_2$. But these coarser particles of lime are afterwards entirely dissolved in the hot solution of calcium chloride, and contribute to form the "base" of the manganese during the blowing. According to the quality of the lime, its degree of hydration and division, and the more or less careful straining, a different excess of it will be required before the manganese reaction ceases to be produced in a filtered sample. The minimum of lime required for this is 1·1, the maximum 1·45 equivalent. It is best, as has been said, not to employ less than 1·6 equivalent of lime; only then is a well-settling mud obtained, from which more calcium chloride liquor can be drawn off than from a mud not settling so well. Thus a stronger mud (containing more $MnO_2$ in a given bulk) is obtained for the chlorine-stills than by employing less lime. This is very important, even more so than a very low base, because it saves coals, acids, space, and labour, and less manganese is lost. Usually from 12 cwt. to 14 cwt. of lime per ton of bleaching-powder are required for the recovery-process (*i. e.* about as much as in the bleaching-powder boxes). These quantities include the portion which is sifted out in making the milk of lime, and which thus does not go into the oxidizer. According to the quality of the lime employed, more is sifted out in some works than in others.

The calcium chloride also plays an important part, probably by dissolving lime. It has been observed that at least two (better 2½) equivalents $CaCl_2$ should be present to 1 equiv. $MnCl_2$, if the oxidizing process is to go on properly; if enough $CaCl_2$ is not present in the liquors, it is purposely added. Especially, "stiff batches" are more apt to be produced when $CaCl_2$ is deficient. According to Post (Ber. d. deutsch. chem. Ges. xii. p. 1541), a solution of calcium chloride of sp. gr. 1·138, such as occurs in the Weldon process, at 60° dissolves 6·37 per cent. CaO, *i. e.* three times as much as pure water.

We now revert to the commencement of the operation in the

oxidizer. Supposing the proper amount of lime to have been added, the *blowing* is continued till the formation of $MnO_2$ ceases.

The colour of the thin mud, at first light yellow, changes into brown and finally into deep black. The oxidation goes on more or less quickly, according to the proportion borne by the volume of air blown in to that of the mass treated; but it is a general experience that the final result is much more favourable when a very strong current of air is applied,—and that a longer application of a less powerful current of air does not act so well, even if the total bulk of air forced through is the same. Hence much stronger blowing-engines are employed now than formerly (p. 204). Of course the efficiency of the blast increases with the depth of the mass to be treated, and with the quantity of MnO contained in a given bulk of the same. Under favourable circumstances an hour's work of 40 to 45 H. P. in the blowing-engine suffices for regenerating as much peroxide as will turn out one ton of 37-per-cent bleach (comp. p. 204). For one ton of actual $MnO_2$, with very good work, 280,000 cubic feet of air are required, containing 58800 cubic feet of oxygen. Weldon cites cases where to a ton of $MnO_2$ 270,000, 158,000, and 180,000 cubic feet of air are required, *i. e.* much less than just stated; but these figures refer to very deep oxidizers. On the other hand, frequently twice as much air is used, viz. 600,000 cubic feet.

When the process is first started, testing has to be performed every half hour during the whole operation, in the manner to be described below, in order to observe whether the formation of $MnO_2$ is still proceeding; this is not necessary afterwards, as it is then known how long it is necessary to blow. In the apparatus formerly worked by the author the limit of this period was reached after three hours; but with other apparatus it may take two hours or five hours, according to circumstances; three to four hours is the average. The alkaline reaction (which must always be sought for in the *filtrate* from a sample) should be quite perceptible for at least an hour after the commencement of blowing; afterwards it is weaker; and it should entirely cease towards the end of this first period. If it ceases too soon, there has been too little excess of lime; if it does not cease at all, there has been too much. But the last-mentioned fault can be corrected in the now commencing final stage by an increased addition of "final liquor." We have seen

above that there must be always a good stock of settled manganese-liquor reserved at a sufficient height.

When the $MnO_2$ in the mixture no longer increases, some more chloride-of-manganese liquor is run in, without stopping the blast; this is the "final liquor." Its object is to act upon half the lime existing as $CaMnO_3$, according to the equation

$$2CaMnO_3 + MnCl_2 + H_2O = CaMn_2O_5 + Mn(OH)_2 + CaCl_2,$$

and thus to reduce the base, by obtaining, without using more lime, more protoxide of manganese, which is afterwards converted into a higher oxide. The final liquor is first added until the filtrate from a sample of the mixture gives the brown manganese reaction with bleach-liquor; this reaction ceases after a few minutes, all dissolved manganese having been precipitated. Then a little more final liquor is added, and the blowing continued till the filtrate from a further sample ceases to be coloured by bleach-liquor; and this is continued till it is seen, from the time which it takes to "blow out" the manganese, that the limit is reached. Now the blowing is continued a little longer, till the filtrate remains undoubtedly clear when bleach-liquor is added; and at last the whole contents of the oxidizer are discharged into one of the settlers. In the author's case this final period regularly lasted 1½ hour; so that the whole operation, from commencing the blowing proper to running off, took 4½ hours. If even the first final liquor cannot be easily "blown out," it is a sign of too little lime; if, on the other hand, very much final liquor is used, there has been too much lime; and these things have to be rectified in the next batch. The total amount of $MnO_2$ per cubic foot is not always increased in the final stages; sometimes it is even lowered; but the base is always diminished.

The progress of the oxidation will be made clear by the following statements. Commencing with a manganese-liquor containing $MnCl_2$ corresponding to 3·2 lb. $MnO_2$ (=*possible* $MnO_2$), this would be diluted about ¼ by the steam and the milk of lime. After one hour's blowing 1·02 lb. $MnO_2$ per cubic foot is found; after 1½ hour, 1·6 lb.; after 2 hours, 1·85 to 2·05 lb.; after 2½ hours, 2·05 to 2·3 lb.; after 3 hours about the same quantity. The base is now about 0·8 or 0·9. Now the final liquor is added; and after 4½ hours there are 2·25 to 2·3 lb. $MnO_2$ per cubic foot; the base is =0·67.

Below 0·6 base it is not easy to get; above 0·75 the work is decidedly bad. The above strength would correspond to about 80 per cent. of all the manganese being present as $MnO_2$, the remaining 20 per cent. as MnO.

All that now remains is the concentration of the manganese mud, which otherwise would become indefinitely diluted by the acid, the milk of lime, etc. The contents of the oxidizer are run past the valve *n*, through the main pipe *e e*, into one of the mud-settlers S S (figs. 73–75). Under normal conditions the thin mud separates after a few hours into a clear solution of calcium-chloride liquor and thicker mud; waiting for several days would not make much difference, and would require much more plant and ground. The clear liquor is drawn off by the pipe *i*, turning round a swivel inside the settlers, and continued outside. When it is in its upright position, nothing runs out; and by gradually lowering it the clear $CaCl_2$ liquor can be run off without disturbing the sediment. The $CaCl_2$ liquor ought never to be run to waste straight from the settlers, but should always pass through a catch-well, say one or two large tubs, in which the movement of the liquor is very much retarded; at the bottom of these tubs gradually a good deal of peroxide mud accumulates. The thicker mud contains at least twice, and may even contain three times as much $MnO_2$ as the thinner (up to 7 lb. per cubic foot); it is still liquid enough to be run for a hundred yards in 4-inch pipes, if this should be necessary from local circumstances.

The operations in the oxidizer may be represented in the following way, neglecting the fact that from the commencement the liquor contains some calcium chloride. All numbers are to be understood as denoting equivalents, not simple weights.

1st operation: Charging the oxidizer and adding the lime.

$$100\,MnCl_2 + 160CaO = 100MnO + 60CaO + 100CaCl_2.$$

2nd operation: Blowing.

$$\begin{aligned}100MnO + 60CaO + 86O \\ &= 86MnO_2 + 14MnO + 60CaO. \\ &= 48CaO,MnO_2 + 14MnO,MnO_2 + 12CaO,2MnO_2. \\ &= 86MnO_2 + 74(CaO \text{ and } MnO).\end{aligned}$$

3rd operation: Adding the final liquor.

$$48CaO,MnO_2 + 24MnCl_2 = 24CaO,2MnO_2 + 24MnO + 24CaCl_2.$$

4th operation: Second blowing.

$$24MnO + 12O = 12MnO,MnO_2.$$

Apart from calcium chloride, there remain:—

| | |
|---|---|
| from the 2nd operation, | $14MnO,MnO_2 + 12CaO,2MnO_2.$ |
| „ 3rd „ | $24CaO,2MnO_2.$ |
| „ 4th „ | $12MnO,MnO_2$ |
| altogether | $26MnO,MnO_2 + 36CaO,2MnO_2.$ |
| or | $98MnO_2 + 36CaO + 26MnO.$ |

Hence upon 100 equivalents of manganous oxide originally employed, and 24 added later on, there are obtained:—

1st, 98 equiv. $MnO_2$, instead of 124 possible, *i. e.* about 79 per cent.

2nd, 62 equiv. bases, viz. 36CaO and 26MnO.

By adding the final liquor the proportion of $MnO_2$ to MnO has been lowered from 86 to 79 per cent.; but the bases have been diminished even more, viz. from 74 to 62.

Now and then in oxidizing two faulty kinds of operations occur, which are very awkward, and spoil the batch. Batches thus affected are known as "red" or "foxy," and "thick" or "stiff." A *red batch* happens when the mixture turns brown-red instead of black. In this case nearly all the manganese is present as $Mn_3O_4$, or only 25 per cent. of all possible $MnO_2$ is present as such, 75 per cent. as MnO. This kind of thing occurs when the blast is working at full strength before any excess of lime has been added to the liquor. When once a charge has turned red, there are no means known of putting it right: no amount of blowing increases the $MnO_2$; and nothing is left but running off the batch and using it up in the stills, where it takes very much acid and yields very little chlorine. The fact is that, in the absence of lime or other soluble protoxide, $Mn(OH)_2$ treated with air in the wet way at a temperature of 60° or so, oxidizes only to $Mn_3O_4$, which is the most stable of all the oxides of manganese, and is incapable of absorbing more oxygen in the wet way.

*Stiff batches* mostly occur under opposite conditions, viz. when the blast is not strong enough, but sometimes under unknown and unexplained circumstances. A stiff batch is known by the fact that the blowing-engine all at once commences to labour very

heavily, the pressure indicated by the gauge on the air-vessel increases rapidly, and at last the engine stops entirely. This rarely happens, except at the commencement of an operation—apparently when too much lime is added, more than can combine with or replace the manganese, or more than the force of the blast can manage. In this case peculiar crystalline compounds are formed, which produce a thickening, or even a complete solidification of the mass. This happens more frequently with still-liquor from native manganese, on starting the process, when more lime is needed; for this reason the *second* addition of lime in this case ought to be made by instalments, which with liquors from recovered manganese is neither necessary nor advisable. A further cause of stiff batches is, heating the manganese-liquor too much before adding the lime. It once happened to the author when the liquor had, by mistake, been got up to 77° C. 55° C. are sufficient; and 65° C. ought never to be surpassed. The temperature always rises a few degrees during the blowing, in consequence of the oxidation, in spite of the considerable cooling by the air blown in. The appearance of a stiff batch is that of lime slaked to a pasty condition only. Sometimes the whole operation must be interrupted, the stiff mass dug out of the oxidizer, and dissolved out of the pipes with acid. But it very rarely goes so far as that; it seems to have happened only at first, before it was known what has to be done when a batch gets stiff. The only remedy is, putting all available steam upon the blowing-engine, and at the same time running fresh manganese-liquor into the oxidizer to dissolve the excess of lime, till the engine works again quite freely. As a rule such a batch will not come out very good at the last; it mostly shows a very high base (1 equivalent and upwards) and low $MnO_2$ (something like 1·3 lb. per cubic foot), and settles very badly, if at all. With a sufficiently strong blowing-engine and proper treatment with lime, stiff batches do not occur at all. Frequently, however, especially with not entirely settled liquors and too slow working of the blowing-engine, the contents of the oxidizer *froth up* so as to overflow at the top; the only and certain remedy here too is, starting the engine at full force.

Some works have an intermediate vessel between the mud-settlers and the chlorine-stills, in which a mechanical agitator rotates and makes the mud run more freely. This arrangement is

unnecessary with good mud and a moderate distance from the stills; it is then sufficient to rake up the mud in the settlers themselves with wooden rakes. At other works they interpose a pan for heating up the mud before it enters the oxidizer; this saves time, steam, and dilution, but is very troublesome, and consequently very rarely done. At two factories they treat the mud, in special agitating-tubs, with dilute hydrochloric acid before running it into the stills, partly in order to remove the $CO_2$, which has been introduced by badly burnt lime, partly to lessen the base; but this complication of the process easily leads to a loss of chlorine, and consequently is not employed at most of the works.

We shall now describe the *treatment of the recovered manganese-mud in the stills.* First, hydrochloric acid is run into the still to a depth of 2 feet—the hotter from the condensers the better; and then manganese mud is run into the sluice-valves, but not sufficient to generate too strong a current of chlorine, which would blow the water out of the hydraulic lutes. With a little attention a perfectly even current of gas can be produced. The manganese mud is run in till the dark colour of the liquid taken out of the test-cock shows that there is enough of it; steam is then blown in (frequently already before this stage), whereupon the liquor again clears up if acid be present. The limit is reached when at a sufficient temperature the liquid is clear but coffee-coloured (a light yellow colour showing an excess of acid) and, poured upon chalk, does not produce *strong* effervescence. It is of course best to test directly for free acid; this is best done by running in caustic soda from a burette till a permanent precipitate begins to appear (p. 129): $\frac{1}{2}$ per cent. of free acid is normal, 1 per cent. decidedly too much. But the saturation of the acid ought not to go too far; for then undoubtedly some manganese mud would remain behind undissolved, subside along with the neutralizing mud, and be lost. When the proper point has been reached, the contents of the still are run into the lower-situated neutralizing well, and the whole cycle of operations begins anew. Each operation in the stills lasts from 4 to 6 hours.

We will now describe the analytical methods employed in the Weldon process. These have been mostly indicated by Weldon himself; they are described here with a few practical modifications introduced by the author, and adapted to the metrical system. The

rough methods for testing the still-liquor and the contents of the oxidizer have been cited above; we must now explain the more accurate methods for testing the recovered mud for $MnO_2$, base, and total manganese. The reagents required are:—a strong, filtered solution of bleach-liquor (not standardized); a solution of about 100 grams crystallized ferrous sulphate and 100 grams pure sulphuric acid per litre; a standard solution of potassium permanganate—most conveniently made from pure crystals, of seminormal strength, *i. e.* 1 cub. centim. corresponding to 0·004 gram oxygen or 0·02175 gram Mn., identical with that employed in testing nitrous vitriol (Vol. I. pp. 56 and 63*); a normal solution of oxalic acid (63 grams per litre); a normal solution of caustic soda (31 grams NaOH per litre).

In testing for $MnO_2$, 20 cub. cent. of the iron solution are pipetted into a beaker, diluted with cold water to 100 or 200 cub. cent., and standardized by the permanganate solution; this suffices for the whole day. Another 20 cub. cent. of the iron solution are treated with 10 cub. cent. of manganese mud. This is taken out of the well-shaken sample-bottle with a pipette, which is then washed outside; its contents are run into the iron solution, and the pipette rinsed out into the same by means of the washing-bottle. The beaker being shaken, the mud is dissolved in a few seconds; the liquid is then diluted, and titrated back with permanganate. The number of cub. cent. used, deducted from that used for the iron alone, corresponds to the $MnO_2$, and at once yields its quantity per litre on being multiplied by 2·175. If, as usual in England, it is preferred estimating the $MnO_2$ in pounds per cubic foot, a pipette containing ½ or 1 cubic inch is employed, and the following formula serves for calculating the result (for one cubic inch):—

$$MnO_2 = \frac{0{\cdot}02175 \times 1728}{453{\cdot}5} x = 0{\cdot}0830x,$$

where $x$ means the number of cub. cent. of seminormal permanganate, found by subtracting those employed for retitrating from those employed in standardizing the iron solution. The number of

* This is more convenient for use than the potassium dichromate proposed by Weldon.

pounds per cubic foot is found from the number expressing the grams per litre by multiplying the latter by 0·0624*.

The "base," as we know, comprises all constituents of the mud which neutralize acid, leaving behind pure $MnO_2$. The base may be lime, magnesia, or protoxide of manganese; the mutual proportion of these bodies influences neither the analytical operation nor the consumption of acid in the chlorine-stills; hence, as a rule, only the total base is sought, in the following way. Twenty-five cubic centims. of normal oxalic acid (with a very high base this is too little) are diluted to about 100 cub. cent., and heated to 60° or 80° C.; 10 cub. cent. of manganese mud are added, with the above-mentioned precaution of washing the pipette &c., and heat applied till the precipitate has become pure white, not cream-coloured—which usually takes less than one minute. Then it is retitrated with standard caustic soda, in order to learn the number of cubic centims. of oxalic acid consumed; the exact determination of the point of neutralization is not very easy, because litmus, even in excess, does not give a very sharp indication. Hence the statements of factory-chemists about their Weldon base are not always trustworthy. The object is attained much more accurately and not much more slowly if the whole is diluted to 202 cub. cent. (where 2 cub. cent. correspond to the bulk of the precipitate), passed through a dry filter, and 100 cub. cent. of the filtrate retitrated with caustic soda, when the indication, in the absence of a precipitate, is much sharper. The oxalic acid acts in this way: first it decomposes with all the $MnO_2$ into $MnO$ and $CO_2$; consequently for each cub. cent. of seminormal permanganate, $\frac{1}{2}$ cub. cent of oxalic acid will be consumed for this object. Exactly the same quantity is consumed to form an oxalate with $MnO$; and a further quantity is consumed for saturating any $MnO$ present over and above that produced from $MnO_2$, as well as $CaO$, $MgO$, $Fe_2O_3$, &c. The latter is the quantity sought for; and it is found

* The accuracy of the permanganate-iron test has been disputed by Post (Ber. deutsch. chem. Ges. xii. p. 1539). He obtained by Bunsen's iodine test results 10 per cent. lower than the above test indicated. But in very careful special comparative trials instituted by the author the results of the permanganate, the bichromate, and the iodine test were found identical. His experiments (as well as those on the testing of Weldon mud generally) are described in the Chem. News, vol. xli. p. 129.

by deducting from the number of cubic centims. of oxalic acid consumed that of the cubic centims. of permanganate found in titrating for MnO: the remainder is equal to the base; and the proportion to MnO is found by dividing this remainder by *half* the cub. cent. of permanganate (as this is seminormal and the oxalic acid normal).

Suppose the litre of the iron solution to have been found = 28·0 permanganate. After running in 10 cub. cent. of manganese mud, only 11·5 permanganate have been required; hence $x = 16{\cdot}5$, and the strength of the mud = 35·88 grams per litre, or 2·24 lb. per cubic foot. 10 cub. cent. of mud are heated with 25 cub. cent. oxalic acid, diluted to 202 cub. cent.; 100 cub. cent. filtered require 1·6 normal caustic. The difference between twice this and 25, = 21·8, gives the total oxalic acid consumed. Deducting from this 16·5 (the above $x$) for $MnO_2$ leaves 5·3 for base. The proportion ($\frac{1}{2} \times 16{\cdot}5 =$) $8{\cdot}25 : 5{\cdot}3 = 1 : 0{\cdot}642$ shows 0·642 to have been the base.

Jurisch (Chem. Industrie, 1880, p. 193) estimates the base by dissolving the mud in standard hydrochloric acid in the presence of ammonium oxalate, and retitrating with standard potash solution.

The total manganese in the mud is estimated only now and then, both because it takes a little more time and because it is not of such importance as the total base. It is, however, very interesting, and must be done from time to time. 10 cub. cent. of mud are boiled with HCl till all the chlorine is driven off, the free acid exactly neutralized by caustic soda, and the liquor again raised to the boiling-point; a clear filtered solution of bleaching-powder is added till the liquid shows a pink colour, from the formation of a trace of permanganate. Apart from this trace, now *all* the manganese is in the state of a precipitate of $MnO_2$; this is thrown upon a filter, completely washed till the filtrate gives no more reaction with potassium iodide, the precipitate dissolved in the acidulated solution of ferrous sulphate, and retitrated by permanganate, precisely as in estimating the $MnO_2$ existing as such in the mud.

*The yield of bleaching-powder* to be got by the Weldon process depends mostly on the quantity of hydrochloric acid condensed, much less on the completeness of the neutralization in the chlorine-stills, which may go up to $\frac{1}{2}$ per cent. free HCl, and rarely exceeds

1 per cent. This figure remains the same whether the mud contains more or less $MnO_2$; and, accordingly, the more pounds of $MnO_2$ per cubic foot the recovered mud contains, the less HCl will be lost. The yield of hydrochloric acid differs very much in different works, according to the construction of the decomposing-furnaces and the better or worse arrangements for condensation; and consequently a works may turn out more or less bleach from a ton of salt than another, without reference to its better or worse recovery of manganese. The latter is certainly also of the last importance; according to the way in which the recovery is conducted, the same quantity of hydrochloric acid will yield much or little bleaching-powder. Where the best possible condensation of acid, the employment of blind roasters (permitting the use of the roaster-acid as well), and a good management of the recovery-process are combined, a ton of 37-per-cent. bleach can be made from 48 or 49 cwt. of common salt (containing 94 per cent. NaCl). The author has also seen the returns of various Lancashire works, showing an average of 53½ cwt. of salt. Even at a works where open roasters are employed and only the pan-acid is consumed for chlorine-making, a production of one ton of bleach from 63 cwt. of salt has been reached; but the average in that case is 70 to 80 cwt. The latter yield should always be reached, even with pan-acid alone, unless a large portion of the latter gets into the post condensers and is thus lost.

If the hydrochloric acid condensed is taken into account by itself, there is a pretty general agreement that a ton of 37-per-cent bleach can be made from 4600 to 4800 litres (=160 to 170 cub. feet) hydrochloric acid of sp. gr. 1·12. This means an average of 24 cwt. of HCl, whilst the chlorine of 37-per-cent. bleach only corresponds to 7¾ cwt; hence little over 30 per cent. of the chlorine of the hydrochloric acid is utilized, though that is more than was utilized by the old process*.

Another matter requiring attention is the supply of native manganese to make up the loss of manganese-liquor. In this respect also the various factories differ very much; but by more careful manipulation this loss is constantly decreasing. Some factories,

* At Aussig, where acid of 33° Tw. is employed, 3½ tons of it are required for 1 ton of strong bleaching-powder = 1155 parts HCl to 1000 bleach, or a little over 23 cwt. to the ton.

formerly losing 5 per cent., now lose only 2½ per cent., or even only 1½ per cent. manganese; but with careless work as much as 10 per cent. may be lost. Apart from purely mechanical losses, attributable to downright slovenliness, care must be taken not to leave any more $MnCl_2$ in the neutralizing mud than is absolutely unavoidable. The better the liquor is neutralized in the stills themselves by manganese mud, the less calcium carbonate will be necessary outside (comp. also p. 214). Theoretically, for making one ton of 37-per-cent bleach, 9¼ cwt. of regenerated $MnO_2$ are required; but practically, owing to the unavoidable loss of chlorine, about 10 cwt. are needed, which are contained in about 500 cubic feet of good manganese mud as it comes from the oxidizer.

It has been noticed that the chlorine from recovered manganese acts much more quickly upon the surface of the lime in the chambers than that from native manganese, and that consequently in the former case the depth of the layer cannot be made so great as in the latter, say in the proportion of 8½ to 10. Whether this is really the case, does not seem to be entirely proved. At one of the largest factories, for each ton of bleach per week to be made by Weldon's process 200 square feet of chamber-floor are assumed. In any case the bleach made by this process is of excellent quality, up to 39 per cent., and is said to lose less in the casks than that made by the old process (about ½ per cent. against 1½ per cent.).

The *cost of labour* in Weldon's process is not much larger on a large than on a smaller scale, of course apart from the cost of preparing the lime and packing the bleach. There is always one man per shift needed for oxidizing (who can also undertake the general supervision), one man for making the milk of lime, one for the mud-settlers, one for the Weldon stills, one for the neutralizing-wells, one for the native-manganese-stills, and one for the steam-boilers. With this staff the manganese may be recovered and chlorine generated for 15 tons of bleach per day; but even if only 5 tons be made, not much less labour will be required—only that employed in lime-slaking, wheeling of coals and cinders, &c., will be reduced. Usually the whole labour is let to a gang of men at so much per ton of bleach, at prices differing according to the size of the works.

*The cost of bleaching-powder* by Weldon's process can be seen

from the following statement of results of working extending over a long period :—

| | £ | s. | d. |
|---|---|---|---|
| Lime, 27 cwt., at 16*s*. per ton ............ | 1 | 1 | 7 |
| Limstone, 5 cwt., at 10*s*. per ton ......... | 0 | 2 | 6 |
| Coals, 25 cwt., at 12*s*. per ton ............ | 0 | 15 | 0 |
| Manganese, 1 cwt., at 100*s*. per ton ...... | 0 | 5 | 0 |
| Casks ............................................ | 1 | 0 | 0 |
| Wages ........................................... | 0 | 10 | 0 |
| Cost of 1 ton 37-per-cent. bleach ... (without general expenses). | £3 | 14 | 1 |

The following is another authentic cost-account (of 1874, when materials were still very costly), from a works at St. Helens :—

| | | | |
|---|---|---|---|
| 15¼ cwt coals, at 9*s*. ........................ | 0 | 6 | 10½ |
| 11¾ cwt. lime for oxidizer, at 18*s*. 6*d*. ... | 0 | 9 | 10½ |
| 11½ cwt. lime for powder, at 20*s*. ......... | 0 | 11 | 6 |
| 6½ cwt. limestone dust, at 10*s*. ............ | 0 | 3 | 3 |
| 1¼ cwt. manganese, at 130*s*. ............... | 0 | 8 | 1½ |
| Wages (including boilermen and bleaching-powder) ............................... | 0 | 17 | 8½ |
| Casks ........................................... | 0 | 17 | 1 |
| | £3 | 14 | 5 |

Cost, inclusive of general expenses, Liverpool commission, &c., f. o. b., £6 5*s*. 0*d*. (at that period).

The cost of recovering as much manganese as suffices for producing 60 tons of strong bleach per week, was stated in 1870, by a large Widnes works, at :—

| | | | |
|---|---|---|---|
| 60 tons lime, at 12*s*. ........................ | 36 | 0 | 0 |
| Slaking and sifting the same .............. | 6 | 0 | 0 |
| 12 tons limestone, at 8*s*. 6*d*. .............. | 5 | 2 | 0 |
| Steam .......................................... | 12 | 10 | 0 |
| Wages for engine and oxidizing ........... | 2 | 16 | 0 |
| Wages for neutralizing and pumping the manganese-liquor ......................... | 1 | 19 | 0 |
| Carried forward ....................... | 64 | 7 | 0 |

| | £ | s. | d. |
|---|---|---|---|
| Brought forward | 64 | 7 | 0 |
| Wages for making and pumping milk of lime | 3 | 0 | 0 |
| | £67 | 7 | 0 |
| Deduct 2*s.* per ton saving in labour on making the bleach | 6 | 0 | 0 |
| | £61 | 7 | 0 |

This is £1 0*s.* 6*d.* per ton of 37-per-cent. bleach, exclusive of interest, management, and repairs. But at that time one third too much lime was used; and the cost of sifting it has been entirely saved, so that now the cost of recovery is only 15*s.* 6*d.* exclusive, or 20*s.* inclusive of interest &c. per ton of bleach.

At Dieuze in 1878 (private information) the following quantities of substance were required for 100 kilog. of bleach 108° G. L.:—

| | | |
|---|---|---|
| Manganese (58 per cent.) | 2·9 | kilog. |
| Hydrochloric acid, 32° Tw. | 397 | „ |
| Lime for the chambers | 60 | „ |
| Lime for the oxidizers | 65 | „ |
| Limestone for neutralizing | 16 | „ |

The consumption of coals, on an average of all works (communication from Mr. Weldon, 1878), amounts to 16 cwt. per ton of 38-per-cent. bleach; but one works in France manages with 9 cwt. In neither case is the burning of the lime included.

For the *calcium chloride* which is obtained in such enormous quantity in the Weldon process, no use has hitherto been found to any considerable extent. As it is quite free from iron, it can be obtained by evaporation and fusing as a perfectly white mass, similar to caustic soda, and, like this, is packed in sheet-iron drums. It is employed at alizarine-works, at some sugar-works as an addition in saturating, for making barium chloride from barium sulphate and coal, for making pearl hardening (Vol. II. p. 576); but most of the $CaCl_2$ solution runs away to waste. It is quite harmless, but renders the water hard wherever it comes. It has been proposed (*e. g.* by Hargreaves, Chem. News, xvi. p. 131) as an addition to manures in order to precipitate the phosphoric acid and keep it from being washed away, also as an antifermenting

and antiseptic substance which at the same time fixes the more volatile ammonia compounds as chloride. The dark brown liquors from boiling esparto or wood-pulp, if on account of the expense of fuel they cannot be worked for recovering the soda, at least can be deprived of nearly all organic substances by precipitation with $CaCl_2$; and the resulting liquor, containing much NaCl, but very little coloured, can be run into watercourses without any fear. Of course, if at any time the efforts of Solvay and others to recover hydrochloric acid from calcium chloride in an economical way should be successful (see Vol. II. p. 172), their processes would be just as applicable to the calcium chloride from the Weldon process as to that from the ammoniacal soda-process.

In 1877 there were 50 Weldon plants at work in England, Scotland, and Ireland, turning out about 105,000 tons of bleaching-powder or its equivalent in chlorate of potash. This is about 90 per cent. of all that is manufactured in Great Britain. In France there were 8 plants, turning out 20,000 tons of bleach and chlorate, being all that was made in that country; in Germany 7 or 8, Austria 2, Norway 1, Belgium 1. Except that in Germany there is one Deacon plant, all the bleaching-powder made on the continent is made in this way.

### *Weldon's Magnesia Chlorine-process.*

We have seen above that the chlorine-process of Weldon now in general use utilizes only about 30 parts of the chlorine contained in 100 parts of HCl as bleaching-powder; the remaining 70 parts run away as $CaCl_2$ in a useless, though harmless, form. Since this is still better than in the old process, probably it would have been acquiesced in without demur, had it not been for Deacon's process (to be described in the next chapter), which came out soon after Weldon's, and which proposed to utilize *all* the chlorine of the HCl. Altogether Deacon's process appeared to be so much more simple and profitable than that which Weldon had worked out to a successful end by untiring energy in the course of years, that for some time it was thought the latter would be supplanted by the former. This incited Weldon to seek a new form of his process which could compete with Deacon's; and thus he arrived at working out his magnesia process. The germ of this is found in previous proposals, *e.g.* that of Binks and Macqueen; but this cannot detract from Weldon's merit of having converted a crude idea, quite

useless in that form, into an actual working process. The new process was carried out by a factory in Lancashire and two in Scotland; but before the unavoidable initial difficulties had been overcome, it had become certain that Deacon's process had not yet assumed a practicable shape. When the fear of competition with Deacon had vanished, Weldon had no inducement to devote more time and capital to the new process. Moreover the following circumstance came into play. The chief advantage of the new process was to be, that by it much more than twice the quantity of bleach could be made from the same quantity of common salt as by the old process, viz. one ton of strong bleach from 25 (or even from 16) cwt. of salt, against about 50 cwt. in the present process. But, as it is, by this latter process so much bleaching-powder is made that its price has been enormously lowered, and the quantity now produced can only be sold with difficulty. If more than twice as much bleach were made, it could not possibly be sold, and its price would fall correspondingly. Consequently the manufacturers do not care for the new process; but if once a large new outlet for bleach or for hydrochloric acid in some other shape should be found, probably Weldon's magnesia process will be brought forward again, for which reason we will now describe it in some detail.

The process is commenced by saturating ordinary acid still-liquors with magnesite or calcined magnesia; this may be done in cast-iron pans or stone vessels. The mixed solution of $MnCl_2$ and $MgCl_2$ is settled, the sediment of ferric oxide, alumina, and gypsum removed, and the solution boiled down in an iron pan fired from below nearly up to the point where the $MgCl_2$ would decompose and give off HCl gas, viz. up to about 160° C. By opening a cast-iron valve the liquid contents of the pan are run into a muffle furnace exactly like a blind roaster for sulphate, consisting of two compartments which communicate by an iron door movable from the outside by chain and pulley. In the first compartment the mixed solution is dried down, during which it evolves HCl with a little free Cl, which are condensed in ordinary condensers. When the residue is nearly dry, in which state it consists of manganous chloride (mostly anhydrous), magnesium chloride (partly as hydrate), a little magnesia, and perhaps a little manganous oxide, it is prevented from caking together to a single hard mass by frequent stirring; and the mass, thus converted into thin cakes,

is pushed through into the second compartment, where it is calcined in the presence of air. Instead of one furnace with two compartments, two distinct furnaces are preferable, the "drying-down furnace" and the "gas-furnace," as the fires in them must be regulated in quite different ways. In the gas-furnace the process is conducted in such a way that free chlorine is given off mixed with nitrogen and an excess of air and a little HCl, while basic magnesium manganite, $Mg_2MnO_4$, remains behind. But for this purpose the temperature must be most carefully regulated, so that, on the one hand, all chlorine is driven off, and, on the other hand, the temperature is not increased to the fusing-point of the mass—which would in that case lose its loose state, causing the further oxidation almost entirely to cease. The best temperature is said to be a "blood-red heat." There is most danger so long as any undecomposed magnesium chloride is present along with MgO and $MnCl_2$. Only as the $MgCl_2$ decomposes may the temperature be increased more and more. At the same time with the magnesium chloride the manganous chloride is also decomposed, by the following reactions :—

1 A. $MgCl_2 + H_2O = MgO + 2HCl$;

1 B. $MnCl_2 + H_2O = MnO + 2HCl$;

2 A. $MgCl_2 + O = MgO + 2Cl$;

2 B. $MnCl_2 + O = MnO + 2Cl$.

The reactions 1 A and 1 B chiefly take place in the first (drying-down) furnace, 2 A and 2 B in the gas-furnace. By a further excess of oxygen the MnO is oxidized further; but, in consequence of the presence of magnesia, not the compound $Mn_2O_3$ or $Mn_3O_4$ is formed, as might otherwise be expected, but a magnesium manganite, $2MgO,MnO_2$ or $Mg_2MnO_4$. This, when properly made, is a dense, black, finely divided powder. However, the manganese is never all oxidized to peroxide; so that along with MgO there is always a certain quantity of MnO present as "base," just as in the present Weldon process. Now and then samples are drawn and tested for peroxide; and when this does not increase any further, the calcining is stopped and the batch drawn out.

The work is practically carried out in this way:—The dried material produced in the first furnace is broken up into thin cakes, pushed through into the gas-furnace and piled up at the end nearest

the drying-down furnace. When a second thin layer of dried material has been produced in the drying-down furnace, the heap of thin cakes in the gas-furnace is moved sufficiently far towards the other end of that furnace to permit this second charge to be pushed through into the gas-furnace, and there piled up as the first had been. Thus at length the gas-furnace is completely filled, and the charges turned over very thoroughly; the material ultimately leaves the far end of the gas-furnace as a finished charge of magnesium manganite.

The magnesium manganite is treated just in the same way as the manganese mud in the present process. It is gradually introduced into a stone still which had been previously charged with the requisite hydrochloric acid; strong chlorine is given off; and a mixed solution of $MnCl_2$ and $MgCl_2$ is obtained, which, if necessary, is again neutralized with magnesia, and with which the cycle is recommenced in the manner described above.

The magnesium manganite may be introduced into the stills in the form of a dry powder; but it is preferably ground under edge-rollers to a mud with a little still-liquor from a previous operation, and gradually run into the still by a hydraulic lute. The work is best carried on in this way:—A little excess of magnesium manganite gets into the still, so that the hydrochloric acid is completely saturated; in order not to lose this excess, but to retain it for the next operation, the contents of the still are allowed to subside a little before running out. At first the manganite mud may be sent into the still in such a way that the acid dissolves it almost instantaneously. When it becomes too weak to dissolve $MnO_2$, it can still dissolve the protoxides (the base) of manganite mud, and thus it can be completely neutralized by an excess of the latter; the liquid then only contains a little undissolved $MnO_2$ in suspension, which, when the settling takes place outside the still, is added to fresh manganite mud; but when the settling takes place in the still itself, the next charge of acid, run in first, dissolves the deposited $MnO_2$, and only after this has been completely done is fresh magnesium manganite run in.

It will be noticed that in this process no waste product at all is turned out (corresponding to the calcium chloride of the other process), and consequently there is no consumption of lime or, in this case, of magnesia, except to make up any accidental loss. Both magnesia and manganese serve only as carriers for atmo-

spheric oxygen to hydrochloric acid, which liberates chlorine. The only material consumed on a large scale is fuel, which, Weldon says, amounts to 30 cwt. per ton of bleaching-powder. All this presents much analogy to Deacon's process, although the principles of the two processes are altogether entirely different.

A considerable drawback of the new Weldon process (though it does not occur to the same extent as in Deacon's process) is the fact that all the chlorine is not given off in the undilute state, fit to be conveyed directly into the absorbing-chambers; this is only the case with the gas evolved with magnesium manganite and hydrochloric acid, while the chlorine obtained in the gas-furnace is strongly diluted with nitrogen, oxygen, and hydrochloric acid. The latter can be easily condensed by cooling-pipes and a spray of water in a coke-tower; and thus sufficiently strong acid for use in the stills is obtained; but there remains the dilution with nitrogen and oxygen. This portion of the gas causes precisely the same difficulties which Deacon's process has to meet for *all* the chlorine gas. Of course, also in the present case the dilute chlorine gas, as in the Deacon process, might be dried by sulphuric acid and brought into contact with a very thin layer of lime in a large series of chambers.

Weldon could not in any case employ this process without infringing upon Deacon's patent; but he disapproved of it altogether on account of costliness of plant and uncertainty of working, and in its place introduced the following:—Either the strong chlorine gas obtained from magnesium manganite is to be mixed with the weak gas obtained from the gas-furnace, and the mixture conveyed into ordinary bleach-chambers [where it probably would not yield any strong bleach], or the strong chlorine is passed directly into the chambers, the weak gas into leaden towers packed with bricks, in which all the chlorine is absorbed by a stream of milk of lime running down. In this case at first bleach-liquor is formed, *i. e.* a mixed solution of calcium chloride and hypochlorite; the further action of chlorine, if the temperature remains low, produces only calcium chloride and free hypochlorous acid:

$$CaCl_2 + CaCl_2O_2 + 2H_2O + 4Cl = 2CaCl_2 + 4HOCl.$$

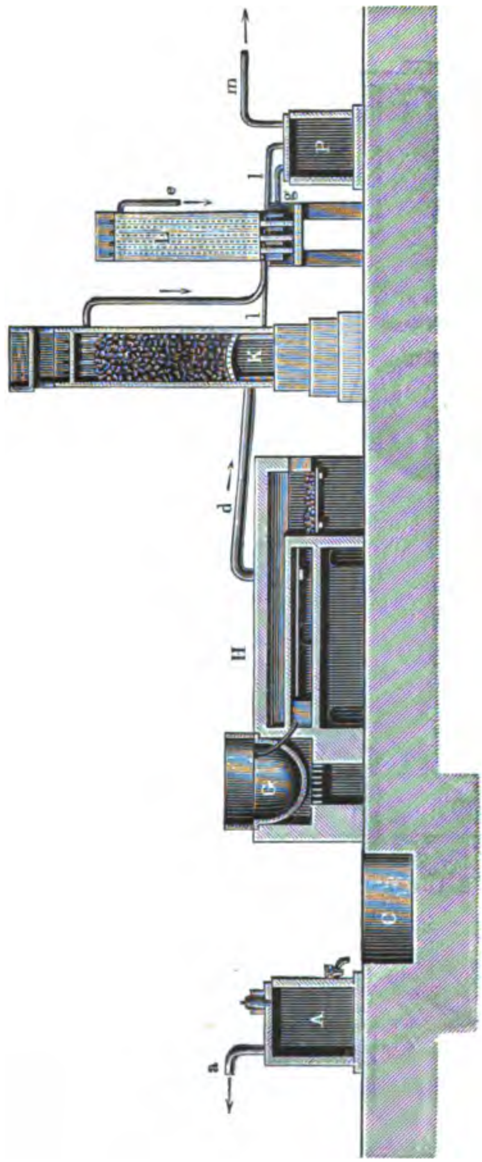
This liquor may be worked for chlorate of potash by boiling it and adding potassium chloride, which may also be done with the first bleach-liquor. In fact calcium chlorate is already formed in the

absorbing-towers, unless the temperature is kept very low. Or the solution of calcium chloride and hypochlorous acid is run into a chlorine-still; and in this *strong* chlorine is liberated by hydrochloric acid:

$$4HOCl+4HCl=4H_2O+8Cl.$$

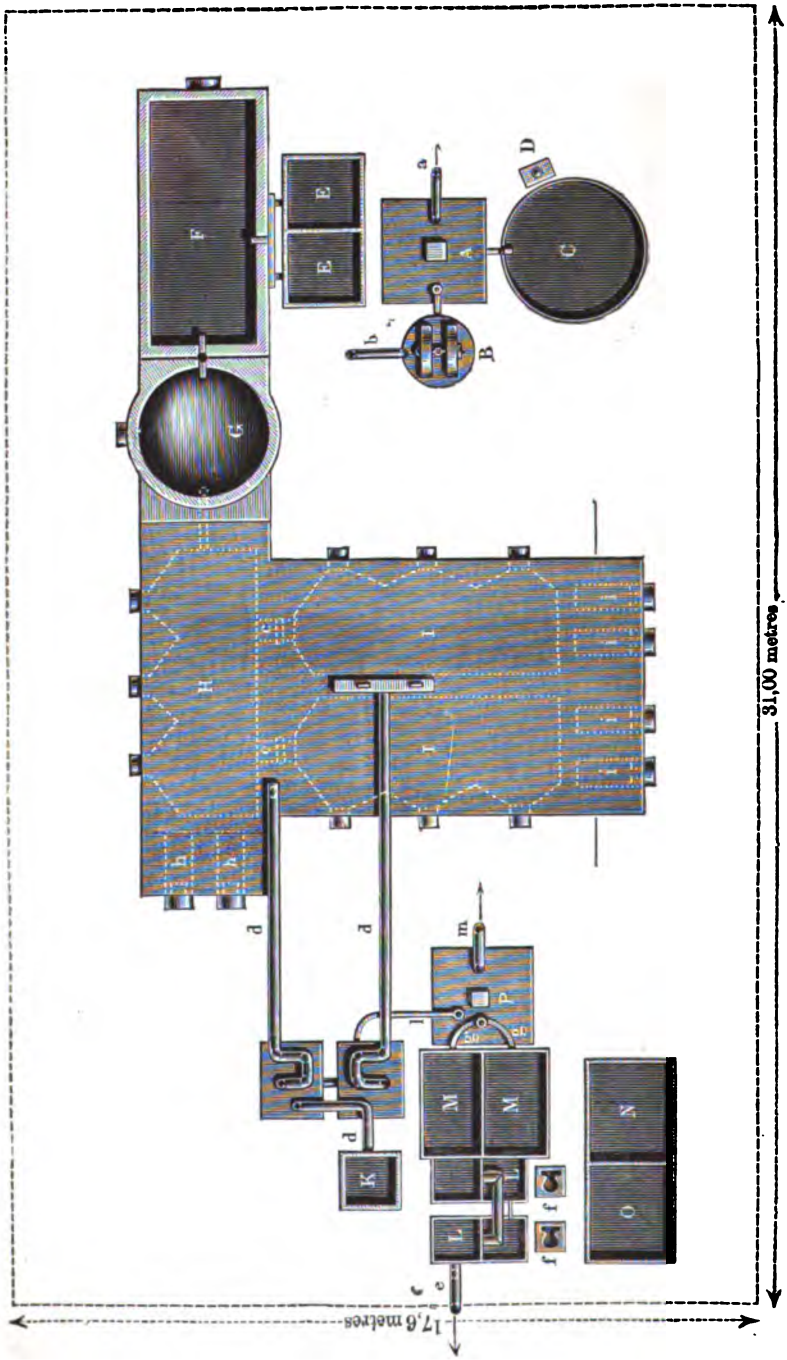
Here only the chlorine of the calcium chloride is lost. But this operation is not quite an easy one; for the evolution of chlorine by the action of HCl upon HOCl is in itself very violent, and in the presence of calcium chlorate, which is very difficult to keep away (in many cases this is formed for the most part along with a little free hypochlorous acid), very explosive chlorine oxides are formed. This drawback might be avoided almost entirely by running the solution in a very thin stream into hydrochloric acid. Actually the process was never carried out up to the formation of free HOCl, but only bleach-liquor ($CaCl_2+CaO_2Cl_2$) was decomposed by HCl; even in this case very weak acid must be employed, which certainly makes its condensation from the gases of the "gas-furnace" all the easier. The simplest plan would be to employ the bleach-liquor as such, which, however, could only be done near the works, on account of the cost of carriage—or to work it for potassium chlorate, the restricted use of which would also prevent a general introduction of this method.

The *apparatus* serving for Weldon's magnesium-manganite process is represented by the sketches fig. 88 (elevation in different vertical planes) and fig. 89 (plan). A is a still for the generation of strong chlorine from magnesium manganite, made just like the mud-stills in the present Weldon process, but turning out much more work, because the magnesium manganite mud may be made as concentrated as desired; *a* is the chlorine-gas pipe, B the mill for preparing the manganite mud, *b* an elevator for the same, above which there is a tank for finished mud; C is a well, of stone or cast iron, for the liquor of $MgCl_2$ and $MnCl_2$; D, the pump, to lift it into the settlers E E. F is a wrought-iron or (better) cast-iron pan for evaporating the same, heated by the waste heat of the furnaces H and I I; G, a cast-iron pot, in which the evaporation is carried nearly to the point where HCl would be given off; H, the "drying-furnace," exactly like an ordinary blind roaster for sulphate, with the fire-places *h h*; it communicates by two channels with sliding doors *c c* with the two "gas-furnaces" I I, built just



in the same way, with the fireplaces *i i*. The two kinds of furnace are connected by cooling-pipes *d d* with a small coke-tower K for

Fig. 89.



absorbing the HCl, from which the washed chlorine gas passes on to the leaden towers L L, loosely packed with bricks and fed with milk of lime; the unabsorbed gases (nitrogen and oxygen) pass through *e* to a chimney. The milk of lime is made in the tank N, collected in O, and pumped up by *ff*. There are two pumps provided because the milk of lime has to be pumped back several times upon the lead towers. The bleach-liqour made in L L collects in the tanks M M (omitted in fig. 88), where it settles, and runs through *g* into the still P, into which also the acid from K runs through *l*; from here again strong chlorine passes away by *m*. The whole apparatus stands on a tight floor, inclined to one side, where an iron pan catches all liquors leaking away.

The dimensions of the various parts of the apparatus, according to Weldon, are calculated as follows (say for a plant to turn out 30 tons of 37-per-cent. bleaching-powder per week, at 829 lb. of chlorine per ton, or 3553 lb. per 24 hours) :—

Since the magnesium manganite liberates about one fourth of the chlorine contained in the hydrochloric acid, and of the other three fourths at least 50 per cent. are evolved in the gas-furnace (in reality, Weldon thinks, 70 to 75 per cent. would be yielded), the above 3553 lb. of chlorine, allowing a loss of 5 per cent. of the chlorine liberated, would require per 24 hours a quantity of magnesium manganite containing 1929 lb. of $MnO_2$. The yield of magnesium manganite is at the rate of the quantity containing 370 lb. of $MnO_2$ per quantity of solution of $MnCl_2 + MgCl_2$ containing 1000 lb. of chlorine; therefore a quantity of concentrated solution containing 5213 lb. of chlorine must be dried down to obtain 1929 lb. of $MnO_2$ in the magnesium manganite. This requires, as shown by experience, a furnace of 136 feet area for drying down, and a "gas-furnace" of 264 feet area, reckoning upon a depth of 3½ inches above the furnace-bed; probably much heavier charges and much shorter time of treatment would be employed, and consequently less furnace-space would be required. For evaporating the $MnCl_2 + MgCl_2$ liquors before they enter the furnace, a circular pot like the caustic finishing-pots, of 10 feet diameter, and a boat pan of somewhat larger capacity, would suffice. The condensing-tower K has to manage one third of the acid which goes into the stills, and can be calculated from this. The leaden absorbing-towers for chlorine are 15 feet high and 3 feet square.

The total cost of an apparatus turning out 5 tons of bleaching-

powder in 24 hours was calculated by Weldon in January 1873, with the then prices, at £1140 without condenser—including the condenser and the apparatus for converting weak into strong chlorine, at £2034; but where bleach-liquor or chlorate of potash are made, £650 of the latter sum ought to go to the account of these latter products, not to that of chlorine-making. The plant occupies a comparatively very small space, as is seen from the designs, and can be erected in a very short time.

As far as the *results* of the new process are concerned, Weldon states that the furnaces at Hardshaw Brook, being built by workmen unaccustomed to build close furnaces, leaked considerably; but nevertheless chlorine was *collected* at the rate of a ton of 37-per-cent. bleach per 25½ cwt. of salt. For each 1000 lb. of chlorine entering the drying-down furnace as magnesium and manganese chlorides there were collected 379·22 lb. of free chlorine (weak), 412·65 chlorine as HCl; 49·00 remained as undecomposed chlorides in the magnesium manganite; and 159·13 (or 15·9 per cent. of the total chlorine) were lost as such or as HCl. The magnesium manganite obtained per 1000 chlorine contained 369·44 lb. $MnO_2$, and liberated in the stills 301·49 lb. more (*strong*) chlorine—together with the above 379·22 weak chlorine, 680·71 lb. To this should be added the 412·65 lb. chlorine collected as HCl, which according to Weldon is more than enough for converting the weak chlorine, after absorption by milk of lime, into strong chlorine. Allowing for the quantity of HCl required for decomposing the $Mg_2MnO_4$, a yield of 680·71 lb. strong chlorine was obtained upon 1252·49 lb. entering the still as HCl, *i. e.* 54 per cent. The figures representing actual experience, however, are only those for the acid supplied to the plant and the products collected; so that the statement of a production of 1 ton of chlorine from 25½ tons of salt is only calculated in an indirect way, and was not observed directly. According to Weldon, when the chlorine absorbed in milk of lime can be used as bleach-liquor or for chlorate of potash, absolutely all the chlorine of the hydrochloric acid is got; *i. e.* the chlorine corresponding to a ton of 37-per-cent. bleach is obtained from 15 cwt. of salt; when the plan of absorbing the chlorine as free hypochlorous acid is employed, 20 cwt. of salt, when all the chlorine from bleach-liquor is liberated by the HCl formed in the process itself, 24½ cwt. of salt would be required. The first result would be four times, the last twice as much as with

the present Weldon process. Of lime only 4 cwt., of coals at most 30 cwt., per ton of bleach are said to be required. Finally, even magnesia might be employed for absorbing the weak chlorine; and then not only the magnesia, but also the HCl combined with it might be recovered.

The cost of bleach by this process is stated at not exceeding £2 10*s*. per ton, inclusive of casks: no skilled labour is required. Only now and then a little magnesia must be introduced, owing to the sulphuric acid contained in the hydrochloric acid. From time to time the $MgSO_4$ must be dissolved out of the furnace product; but its value is said to exceed that of the magnesite. [Also when the cost of evaporation is reckoned ?]

Three factories actually put up plant for Weldon's magnesia-process, and made a good deal of chlorine by it; but after a short time all three went out of repair and were replaced by ordinary Weldon plants. Although this proves that the magnesia-process, as to its technical part, has to overcome some difficulties, it seems very probable that with any large demand for HCl or Cl it would come to the front again; probably all those difficulties would have been overcome long since, if any considerable fraction of the sums spent upon Deacon's process had been expended upon it.

# CHAPTER VII.

## THE DEACON CHLORINE-PROCESS.

While Weldon, at the works of Messrs. Gamble & Co. at St. Helens, worked out the process which has made his name known throughout the civilized world, only a few miles away, at the works of Messrs. Gaskell, Deacon, and Co., at Widnes, another chlorine-process was originated, which appeared to inaugarate a much greater revolution of this whole manufacture. Its inventors were Henry Deacon (deceased in 1876), who is usually mentioned alone, and in whose name all patents are taken out, and his chemist Dr. Ferd. Hurter, to whom undoubtedly belongs a large share in working out this process. (Jurisch, in Dingler's Journal, ccxxii. p. 366, calls him "the well-known discoverer of the reactions upon which the so-called Deacon process is founded.") But Deacon himself was not the discoverer of its fundamental idea; he followed in the footsteps of Oxland, Mallet, etc., who have been cited before (pp. 182 & 184). It appears that they commenced working at it in 1867 (Deacon's first patent is dated April 29, 1868); but it was in 1870 that the new process first became more widely known by a paper read by Mr. Deacon at the Liverpool Meeting of the British Association, which at once excited general attention and great expectations. That paper was reprinted in the 'Chemical News,' vol. xxii. p. 157. It starts from the fact, known long before, that a mixture of hydrochloric acid gas and oxygen at a sufficient heat, especially on passing over red-hot porous materials, is partially split up with formation of chlorine and water;

$$2HCl + O = H_2O + 2Cl;$$

but by the employment of certain subtances, over which the mixture is passed, the decomposition was stated to take place at a lower temperature, and so completely that *all* the HCl could be decomposed and its chlorine liberated [this has never been done, nor even approaching one half, on the large scale !]. For this object a substance must be chosen which remains unchanged when the mixed gases pass over it, but influences the changes in the gases. Copper-salts possess this power in a very marked degree; and of these the sulphate is the most convenient. If pieces of common red brick are dipped into a solution of cupric sulphate and dried, filled into tubes and the heated gases passed through, the reaction already sets in at 204° C., and is most active between 373° and 400°; at 427° C. cupric chloride begins to volatilize. Thus an indefinitely small particle of cupric sulphate can effect the liberation of the whole of the chlorine from an indefinitely large mass of hydrochloric acid gas. The activity of the cupric sulphate seems to depend entirely upon its surface. According to the speed of the current of gas more or less HCl is decomposed; but the quantity of chlorine liberated is a constant for the same apparatus, temperature, and time. Even the admixture of indifferent gases, as aqueous vapour, nitrogen, carbonic acid, sulphuric acid, does not change the law. Deacon was led to this observation by theoretical deductions from the previously discovered process of preparing chlorine by heating cupric chloride, oxidizing the cuprous chloride, adding HCl, and again liberating chlorine from the product formed. But his idea differs from this in the important point that he carries on the reactions not successively, but simultaneously, and thus arrives at a continuous process of preparing chlorine. He further found the chlorine gas, diluted with so much nitrogen, to yield strong bleaching-powder if passed over a large surface of lime in such a manner that the strongest gas meets with the most nearly saturated, the weakest gas with fresh lime. Deacon states the reaction itself to be a source of heat, 4 volumes of HCl and 1 of O (*i. e.* 5 volumes) yielding 2 vols. $H_2O$ and 2 vols. Cl=4 volumes; if from the 34,462 units of heat, resulting from the union of oxygen and hydrogen, the 23,783 units are deducted which are required as the combining-heat of chlorine and hydrogen, an excess of 10,679 units of heat remains to be given out. The water and nitrogen present absorb this heat and reduce the apparent temperature; but this evolution of heat is a material assistance in making up for

the loss of heat in the decomposing-apparatus by radiation. [Upon this point a discussion afterwards arose: Thomsen (Dingl. Journ. cxcix. p. 128) charged Deacon with having overlooked that the water formed is not in a liquid but in a gaseous form; Hurter replied in the Berichte der deutschen chemischen Gesellschaft, 1871, p. 199; and Thomsen, ib. p. 596, upheld his first position].

Deacon further states that, in the gases evolved in the ordinary salt-decomposing apparatus, sufficient air is present to liberate all the chlorine; the heat of the gas requires to be carefully regulated, but can be easily kept constant by means of a brickwork regulator and an improved pyrometer. Iron resists the action of chlorine gas very well; the large bulk of the gases causes no difficulty; and the only real, but not very important difficulty is the volatilization of some ferric chloride, which is deposited in the bricks saturated with copper-salt, and must be kept out by a purifying apparatus specially interposed.

Even after the first difficulties appeared to be overcome, Deacon incessantly made new endeavours to clear up the conditions of the process; their results are stated in a lecture delivered before the London Chemical Society (Chem. Soc. Journ. x. pp. 725–767). The following is a brief abstract of them:—

Only such substances exert a "catalytic" action upon a mixture of HCl gas and air as are chemically acted upon by hydrochloric acid, especially those which form chlorides with it decomposable by hot dry air with evolution of chlorine; but the amount of action of the HCl upon those substances is not proportional to the amount of chlorine obtained by continuous action. It is indefinitely small with clays, most pumice stones, ferric and chromic oxides. To obtain the action in the highest degree, the substance must at the same time possess affinity for oxygen at the temperature worked with. The most active substances are the salts of copper—of which the sulphate is always employed, on account of its cheapness. There is always some cupric chloride formed, but fortunately not in sensible quantities, except at a temperature above the most favourable to the evolution of chlorine. Not the mass, but the surface of the copper-salt determines the amount of the reaction. For the same mixtures of HCl and O, and at the same temperatures, the quantity of HCl decomposed by a molecule of a copper-salt in a given time depends upon the number of times the molecules of the gaseous mixture are passed through the sphere of action of the

copper-salt. Inversely the activity of a molecule of copper-salt depends upon the speed with which fresh matter is presented to, and the products are removed from it. In this no force is created, but (as Bunsen says in his 'Gasometry,' Engl. Transl. p. 255) "catalytic action is not an equivalent to the unlimited amount of labour; but for every decomposition effected an equivalent amount of force is absorbed, just as, in the case of a weight raised by a falling body, a force is expended exactly equivalent to the work done." In long parallel tubes of the same diameter, the number of opportunities of action in the same time is nearly the same at all velocities of the current of gas; in similar tubes of different diameters it remains the same when the velocities of the currents of gas are in inverse proportion to the squares of the tubes' diameters. In porous masses the opportunities of action increase with increased velocities of the current of gas in nearly direct proportion. Other conditions remaining the same, the percentage of hydrochloric acid decomposed in any given time varies with the square root of the proportional volume of oxygen to hydrochloric acid. The cupric chloride formed bears no definite proportion to the quantity of chlorine evolved. As the sphere of action includes molecules not in contact with the copper-salt, therefore HCl must be decomposed under circumstances where the union of either element with the copper-salt is impossible; *i. e.* the decomposition must be in part, if not entirely, caused by the resultant of the forces engaged, and therefore direct from $2HCl + O$ to $H_2O + Cl$.

If the truth must be told, the somewhat pretentious theoretical investigations of Deacon, so far as can be seen, have had next to no influence in promoting the practical working-out of the process; the latter has had to be done according to the ordinary homely technical rules. Most chemists will not agree with Deacon in rejecting altogether the explanation of the process from the formation and re-decomposition of cupric chloride; the "catalytical force" is not in great favour now, and can only be invoked where *no* other explanation can be given. This may hold good for clay, pumice, or platinum-black, but not for cupric chloride, the immensely stronger chemical activity of which seems to prove that not only a "resultant of attractive forces," but real chemical combinations and decompositions are at work here. If Deacon had only not been so positively convinced that he had already discovered the

true theory of the process called after him, even to the oscillations of the molecules, there would not have been so many and such costly mistakes made by himself and others, instead of proceeding cautiously with further investigations (Hasenclever, Dingl. Journ. ccxxii. p. 257).

A further contribution to the theory of the Deacon process has recently been made by Hensgen (Dingl. Journ. ccxxvii. p. 369). He starts from his observations on the decomposition of anhydrous cupric sulphate by dry HCl gas (Vol. II. p. 178), and finds that, in the case of simultaneous action of oxygen, the decomposition takes place almost quantitatively according to the equation

$$CuCl_2 + H_2SO_4 + O = CuSO_4 + H_2O + Cl_2.$$

When air was employed instead of oxygen, the decomposition was less complete. Such a mixture of $CuCl_2$ and $H_2SO_4$ is just formed by the action of HCl upon anhydrous cupric sulphate. But when more sulphuric acid is present than is required by the above equation, the HCl is given off so quickly that the oxygen as it arrives has scarcely time to act, and thus but little chlorine is produced (comp. the conclusion of this chapter). The reactions which take place when HCl and air act upon $CuCl_2$ without sulphuric acid, are represented by Hensgen in this way:—

1. $6\,CuCl_2 = 2\,(CuCl_2 + Cu_2Cl_2) + 4\,Cl$;
2. $2(CuCl_2 + Cu_2Cl_2) = 3\,Cu_2Cl_2 + 2\,Cl$;
3. $Cu_2Cl_2 + O = CuO,CuCl_2$;
4. $CuO,CuCl_2 + 2\,HCl = 2\,CuCl_2 + H_2O$.

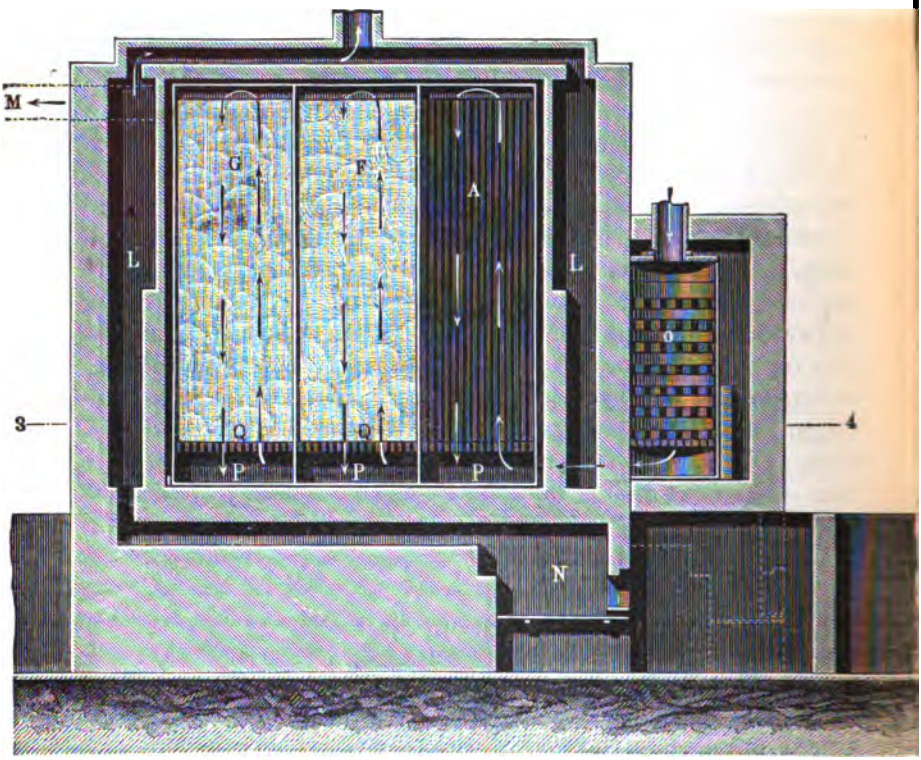
*The practical way of working Deacon's process* is as follows:— The necessary hydrochloric acid gas is taken direct from a decomposing-pan. Deacon recommends getting it in small factories by heating ordinary muriatic acid; but this does not pay, and thus one of the greatest advantages claimed for this process is lost, viz. that the costly plant of coke condensers and the incomplete condensation of HCl in them are avoided by decomposing the gas directly after it has been made. It is true that this direct employment of the HCl gas has the great drawback of preventing the uniformity of the process; for at the beginning of each operation there is a very strong, afterwards only a moderate, stream of HCl given off. In order to equalize this to a certain extent, two pans have been combined in this way:—The strong gas escaping at first

is passed through the Deacon apparatus; when afterwards weak gas is given off, it is condensed in a coke-tower in the ordinary way, and in its stead the first strong gas from a second pan is sent into the Deacon apparatus. But this is just one of the drawbacks of Deacon's process: a gaseous mixture somewhat poor in HCl, as it is given from the pans in the later stage, is ill-adapted for it, and that from blind roasters not at all (the latter, as we shall see, moreover on account of its sulphuric acid); open-roaster gas is entirely out of the question. Thus much of the muriatic acid made in alkali-works is not fit for the Deacon process; it has to be condensed in the ordinary way, and can only be employed for the recovery of sulphur from the tank-waste, bicarbonate, etc., or just for making chlorine by Weldon's process. Hence condensing-towers cannot be dispensed with after all, with all their disadvantages. With Hargreaves and Robinson's sulphate process (Book II. Chap. IV.) the Deacon process is not at all compatible, since in this case *all* the HCl is diluted with a large quantity of nitrogen and air.

The hydrochloric acid gas is always mixed with a certain quantity of *air*, containing more oxygen than is required for decomposing the HCl. It is not necessary to take special care of this, since the gaseous mixture escaping from the decomposing-pans always contains sufficient air, entering through the joints of the doors and dampers. This is checked from time to time by forcing a sample of the mixed gases through a certain quantity of standard soda solution coloured with litmus, by means of an indiarubber finger-pump, counting the number of strokes necessary for turning the litmus red. An exact regulation of the quantity of air is effected by the Root's blower working at the end of the apparatus, which, according to its greater or less speed, will suck in more or less air through the joints of the pan-door.

The mixed gases are now passed through a set of U-tubes in order to be raised to the proper temperature (say about 400° C). The heating-apparatus is quite similar to the hot-blast stoves of iron-works. Then (in Deacon's original apparatus) they pass through the *decomposer*, shown in fig. 90 in section (on the line 1...2), in fig. 91 in plan (on the line 3...4). A...I are cast-iron columns, or rather one large box with partitions, filled with a porous material impregnated with cupric sulphate. The first (and sometimes also the second) column is filled with material vertically disposed; best

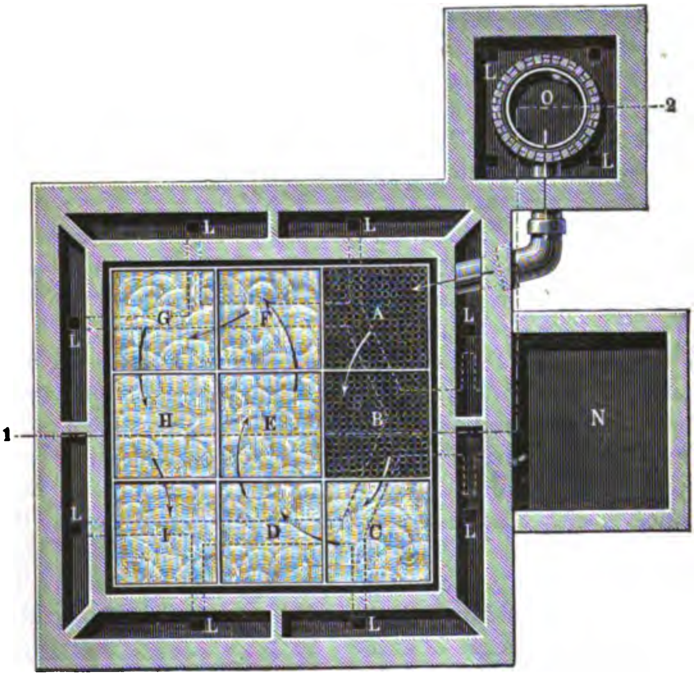
Fig. 90.




of all are common narrow drain-pipes. The object of this is that the dust of ferric chloride or oxide (to be mentioned at once) may fall out more easily. The other columns are filled with impregnated material consisting of small spherical, flat, or irregular pieces of burnt clay, usually clay balls or "marbles" a little over ½ inch in diameter, in order to offer the largest possible surface within the smallest space to the passing gas, without obstructing its passage to such an extent as to make a strong draught necessary. P P are chambers into which the dust collecting among the superincumbent porous material falls through the grating Q, and from which it is removed from time to time.

In the more recent plants the travelling of the current of gases has been facilitated by leaving out the partitions in the decomposer, without any drawback resulting; and consequently the vertical

Fig. 91.




drain-pipes have also been abandoned. According to Jurisch (Dingl. Journ. ccxxii. p. 569), first for one apparatus with ten upright compartments two with five compartments each, and ultimately a single box was substituted, into which the gas enters at one end at the top, and out of which it issues at the diagonal bottom end. Deacon next built an almost spherical apparatus with a conical grate and contrivances for continuously filling and emptying. Ultimately, as we shall see below, cylindrical apparatus, 10 to 12 feet wide and 15 feet high, have been employed, with an inner lining of grate-bars, arranged like Venetian blinds, forcing the gaseous current to pass through an annular space of decomposing-material. It does not appear that the best form of decomposer has been discovered yet; but at present the cylindrical form is preferred also with respect to the prevention of leakage through the joints.

The *dust* accumulating in P P does not, as was formerly believed, chiefly consist of ferric chloride, or ferric oxide formed by its

decomposition, but of ferric sulphate (comp. below). It often causes much unpleasantness and trouble by obstructing the passage of the gases. The ferric chloride is partly formed in the metal U-tubes in which the gas is heated, partly in the decomposing-pans. The first can be prevented by heating the gas in a Cowper or Whitwell stove made of firebricks on the regenerative principle, as now generally used for blast-furnaces. Deacon thinks that by employing wider metal pipes and very moderate heating the volatilization of ferric chloride from this source might be prevented in any case; and the second above-mentioned source of it could be avoided by employing leaden decomposing-pans instead of iron ones [but this no alkali-manufacturer will consent to!].

In front of the decomposer an apparatus O is shown, which Deacon calls the *heat-regulator*. It is made of the same material as the decomposer, and packed with bricks in pigeon-hole fashion. Its function is to obviate any sudden changes of temperature of the gas sent into the decomposer. The heat accumulated in the regulator is either increased by the gases or given up to them, according to whether they are hotter or cooler than the regulator; the latter is separated from the other apparatus, so as not to be influenced by convection of heat. In this way, without any skilled labour, the temperature is said to be kept nearly constant, with oscillations not exceeding 33° C. in 24 hours. Later on Deacon himself did not consider this regulator essential.

The decomposer and the regulator are surrounded by a jacket of brickwork, in which the flues L L, communicating with the fires N N, are laid out. These fire-places and flues serve partly for heating the apparatus to the proper temperature, partly for preventing too great a radiation of heat.

The temperature of the decomposer etc. is ascertained by an improved kind of pyrometer invented by Deacon. Usually tubes of brass and iron are employed for measuring the temperature by their variable expansion by heat; but these soon undergo a permanent change, and then give altogether unreliable indications. Instead of these, Deacon employs solid iron and copper rods, which, according to him, are not liable to those permanent expansions. But it would seem that his pyrometers also are far from remaining trustworthy for any great length of time.

The gases leave the apparatus by the pipe K in the direction of the arrows; they are forced on by a Root's blower (Vol. II. p. 150)

which is placed at the end of the whole system, *i. e.* behind the bleaching-powder chambers. The speed of the gaseous current is regulated by an ether anemometer, to which Hurter had given a similar shape to that shown in fig. 158 (Vol. I. p. 341) before it was otherwise known; but a simple vertical U-tube will do as well.

The mixture of gases leaving the decomposer consists of chlorine, undecomposed hydrochloric acid, aqueous vapour, nitrogen, and oxygen (in excess). They are tested by aspirating a known volume through a solution of sodium hydrate, and estimating first the bleaching chlorine by sodium arsenite, then the total chlorine by silver nitrate. According to Hurter (Dingl. Journ. ccxxiii. p. 71) the decomposition can be made almost complete in the laboratory; but on the large scale it but rarely amounts to 80 per cent. of the HCl, especially when the apparatus have become leaky. Except in quite new and perfectly tight apparatus, a total decomposition of 45 per cent. must be acquiesced in, if the mixture was composed of equal volumes of air and HCl gas with a little steam. The quantity of chlorine produced, if the other conditions remain the same, is nearly proportional to the geometrical means of the quantity of HCl and air present. If the HCl contained in a unit volume of the mixture be called $x$, and the air $y$, the quantity of chlorine Cl, if $c$ denotes a constant, is $\mathrm{Cl}=c\sqrt{xy}$. Since with incomplete decomposition or with a very large excess of air the tension of the chlorine gas produced becomes about $\frac{\mathrm{Cl}}{y}$, we have $\frac{\mathrm{Cl}}{y}=c\sqrt{\frac{x}{y}}$. Hence the tension of the chlorine gas is subject to much smaller variations than that of the hydrochloric acid gas employed for its generation. Usually there is $1\frac{1}{2}$ vol. air present to 1 vol. HCl; this in the case of complete decomposition yields $\frac{1}{2}$ vol. Cl, or with 50 per cent. decomposition (*i. e.* in a *very* good apparatus) $\frac{1}{4}$ vol. Cl, which, mixed with the remaining N and O, yields dilute chlorine with about $\frac{2}{13}$ vol. $=15$ per cent. chlorine. [According to reliable information from one of the few manufacturers still working the Deacon process, the above statements of Hurter's are decidedly exaggerated, if the work extending over a longer time be considered. He himself gets only 30 per cent. of the chlorine contained in the salt, and that with great interruptions; the best works known to him only gets 40 per cent.; at Messrs. Gaskell, Deacon, and Co.'s own works from 50 salt of

93 per cent. NaCl 21 or 22 bleaching-powder of 35 per cent. is made, *i. e.* 26·1 to 27·4 per cent. of the chlorine contained in the salt. These calculations certainly include the loss in absorption.]

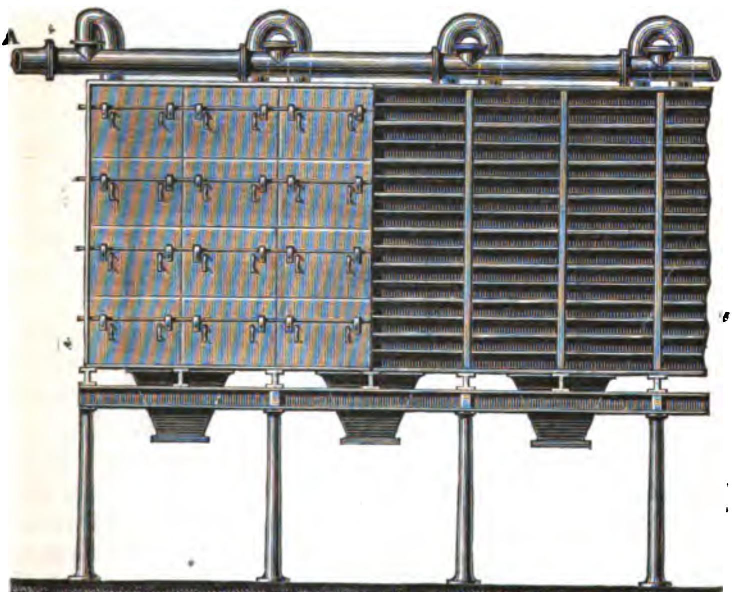
The mixed gases are first cooled by a long series of pipes, either of stoneware or glass; the latter are very suitable for this purpose, as there is no pressure from within; but suction, or a set of Woulfe's-jar receivers, just as in the ordinary continental acid-condensation, may be employed. Then the *hydrochloric acid* is entirely *washed out by water*. The colour of the gaseous mixture permits a rough estimate to be made of the undecomposed HCl present along with the chlorine. A more accurate estimation is effected by forcing the gas through a certain volume of the reagent by means of a finger-pump, as before. It is possible to make the hydrochloric acid pretty concentrated by good contrivances, especially by the help of Woulfe's bottles. According to a patent of Deacon's (of May 8, 1876), undecomposed hydrochloric acid is better utilized by absorbing it in ferric oxide impregnated with cupric sulphate; heated air is passed over it, to liberate chlorine (comp. the process of Mallet, p. 184). This process, if tried at all, seems to have been unsuccessful.

The gases freed from hydrochloric acid, if intended for the manufacture of bleaching-powder, must now be *dried*; but if they are passed into milk of lime, to make bleach-liquor or chlorate of potash, no drying is necessary. Formerly for this purpose a tower filled with calcium chloride was employed. This caused great trouble; and the drying was very incomplete. It is now done by a leaden tower packed with coke, in which strong sulphuric acid trickles down. Deacon states that acid of 144° Tw. is sufficiently strong to absorb the water so far as is necessary for making bleaching-powder; the author has even known acid of only 120° Tw. employed for this purpose. Certainly every trace of water in the dilute chlorine of Deacon's process is injurious and should be removed (Hurter, Dingl. Journ. ccxxiii. p. 429), chiefly because it forms a layer impermeable to the gases in the lime-chambers; it also assists in the formation of calcium chlorate.

The chlorine gas, purified from hydrochloric acid and water, is always so much diluted by nitrogen and an excess of oxygen that its absorption in ordinary bleaching-powder-chambers is not at all feasible. Indeed the largeness of the volume of the gases to be dealt with here seemed to present a great difficulty; it amounts to about

20,000 cubic feet per ton of sulphate. Such a quantity of gas can only be dealt with by continuous absorption by being drawn away as it is formed and completely deprived of chlorine in its passage through the absorbing-apparatus. In order to do this, Deacon employs the hydrated lime in a very thin layer (not above $\frac{5}{8}$ inch), in a series of large *chambers* made of slate or sandstone flags, containing each a number of horizontal shelves at distances of 6 inches from each other. Figs. 92 and 93 show a front elevation and two

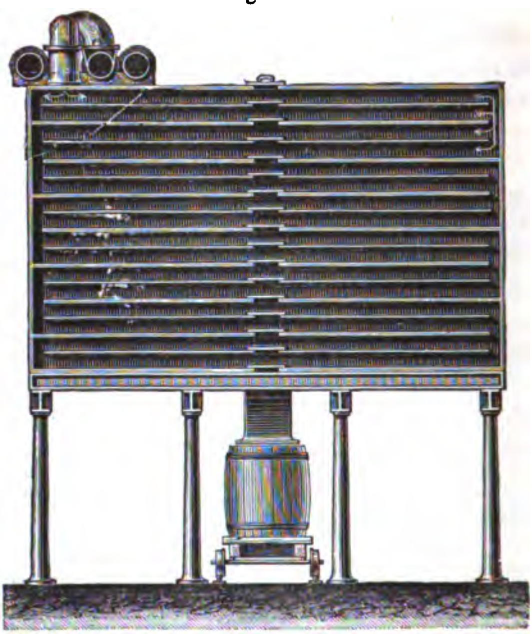
Fig. 92.




sectional elevations of the chambers. In these the gas must pass over a very large surface of lime. By convenient cast-iron distributing-pipes each chamber can be made the first or the last with respect to the current of gas. The gas coming from the drying-apparatus, comparatively rich in chlorine, is passed through the oldest chamber, in which the lime is nearly saturated; at the end of the set the nearly exhausted gas meets with fresh calcium hydrate and gives off its chlorine to this so completely that often

the gas issuing from the Root's blower cannot be smelt at all [but often very perceptibly !]. The first chamber, when it has been completely saturated, is cut off, emptied, charged with fresh lime,

Fig. 93.



and made the last chamber, the fresh gas being moved forward to the next chamber. In this way Deacon has certainly overcome the difficulty of managing such a large bulk of gas; but the first cost of his chambers is enormously high, as they must be built of expensive material and rest on a most substantial foundation; any settling instantly produces a leakage of air inwards through the joints. Another plan proposed by Deacon, but not successfully carried out, was, to have a tower with slanting slate shelves inclined alternately in different directions, the bleaching-powder gradually sliding down upon these by the assistance of a shaft and blades, fresh lime being put in continuously at the top, and finished bleach drawn out at the bottom. The principle of this apparatus is exactly the same as that of Leather (p. 165), patented for ordinary bleach.

Hurter has published an extensive investigation (Dingler's

Journal, ccxxiii. p. 417; ccxxiv. p. 424) of the progress of the absorption of the chlorine by calcium hydrate, the disturbing effects of the foreign gases mixed with the chlorine, and the influence of the heat given off during absorption. Its results are as follows:—The depth of the layer of lime has no influence upon the absorption, but the chlorine simply penetrates down to the same depth in equal times. The lime, being a very fine porous powder, of specific gravity 0·5 (including the air), can be but slowly penetrated by chlorine, because the occluded air cannot escape instantaneously. Thus a slow current is formed, all the slower the more deeply the gas has to penetrate. The absorbing-capacity of the whole absorbent layer when its surface is already covered with finished bleach is only half as much as that of fresh lime. In the beginning of the absorption, but only for a very short period, instantaneous absorption will go on very quickly; then the absorbing-capacity falls to about one half and remains constant till the chlorine meets with the last layer of lime; from this point the absorbing-capacity gradually decreases; and at last, when all the lime has been saturated with chlorine as far as possible, it is zero. The middle period lasts longest, and is practically the most important. On the strength of the above theory and of experiments on a small scale, formulæ have been calculated for the quantity of chlorine absorbed by a unit of space for any given time; and practical experience on a large scale has justified the correctness of those formulæ. The depth of lime allowable was calculated according to them by Hurter at 1·61 centim.; this must be considered the maximum for practical work, for which $\frac{5}{8}$ inch (=1·5 cm.) had previously been stated. The dimensions of the chambers could also be calculated in this way. In order to finish 25 tons of bleaching-powder per week, considering that the lime takes 96 hours to be converted into bleach, at least four chambers must be provided for working, and one for emptying and recharging, if one chamber is to be finished daily. Consequently each set must consist of at least five chambers, each of which must hold as much lime as corresponds to $4\frac{1}{6}$ tons of bleach. As this would be an enormous area, the chambers have been made to come on turn every 16 hours. In order to save connecting-pipes, the gas is conveyed in one chamber from the upper to the lower shelves, in the next from the bottom to the top; each two such compartments form a pair of chambers to be

laid off at a time. Of such pairs $\frac{96}{16}=6$ are required for working, and one more for charging. Indeed Deacon's chamber-set consists of seven pairs with 16 shelves each, on the whole $7\times2\times16=224$ shelves. The 16 shelves of each chamber have an area of 1250 square feet, upon which $18\frac{1}{2}$ cwt. of calcium hydrate can be laid $\frac{5}{8}$ inch deep. Since in a week of 6 days $\frac{144}{16}=9$ pairs of chambers are drawn, this means $2\times9\times18\frac{1}{2}$ cwt. $=16$ tons 13 cwt. slaked lime, which furnish 25 tons of bleach. With good works and higher tension of gas [which but very rarely exists in practice] Hurter's theory and practice yield much more (as much as 33 tons of bleach per week from a Deacon's chamber-set), but with a lower tension of gas considerably less.

Since the slate or sandstone chambers do not conduct the heat liberated in the formation of bleaching-powder (according to Hurter 195 units of heat to each unit of weight of the bleach) so quickly as the lead or iron chambers of the ordinary process, and since in them the process of absorption is even greatly intensified by the large number of shelves, which do not radiate any heat outwards, it is not even possible to employ strong chlorine gas in Deacon's chambers, as the temperature in them would otherwise rise to 70° or 80° C. Hence the chlorine must always be to some extent diluted with inert gases, which in practice is always sufficiently the case.

That it is more advantageous to convey the gas in the absorbing-apparatus in a downward than in an upward direction Hurter had already shown, in a paper mentioned in the chapter treating of the Hargreaves process (Dingl. Journ. ccxxiii. p. 200).

As far as the *consumption of coals* is concerned, Deacon speaks of burning only one ton of coals to make a ton of 35-per-cent. bleach from 32 cwt. of common salt. The cost of producing a ton of bleach, without interest, repairs, general expenses and patent-royalty, was to be £3. Practically it is much higher; and the bleach is frequently worthless, because it is too weak [see below].

So far as the author can make out, there have been built in England twelve, in Germany two plants, in France none, for Deacon's process. From inquiries made, it appears that, of the English works, in 1878 only four, in 1879 only three were going, including Messrs. Gaskell, Deacon, and Co.'s own: the others had

mostly dropped the licence; and several of them had taken down the plant again*. In all those works, and in the remaining four, Weldon plants are employed. The two German works had also been stopped; but one of them is working again. The few manufacturers still working the Deacon process speak with great reserve as to its success; their neighbours, who from the first had stuck to Weldon, congratulate themselves for having saved enormous outlays and still greater troubles and cares. It must accordingly be stated that, in spite of unceasing efforts and pecuniary sacrifices, the Deacon process, promising so much, is still very far indeed from reaching its aim.

How can it be explained that Weldon's process has won a permanent position in the cycle of alkali-making operations, whilst Deacon's process has been so little successful? The success of the latter would have been one of the most splendid triumphs of modern science in its application to industry; and all bleach-makers must regret that they cannot employ a process which in theory, and, as it appeared for some little time, also in practice, possessed such great advantages over Weldon's process. In the latter the hydrochloric acid must be condensed as usual, and its chlorine must be liberated by native or recovered manganese; the still-liquor, again, must be worked for the recovery of manganese, which cannot be done without loss; and a large amount of hydrochloric acid is expended to saturate the lime necessarily added in the recovery-process. For the oxidizing, still-work, and neutralizing, skilled and trustworthy men are required; and, for all that, sometimes "red" or "stiff" batches occur in oxidizing, which consume much acid and give out very little chlorine. It is true that all these drawbacks have not prevented the Weldon process from becoming quite familiar to alkali-makers. But the Deacon process promises much more. While in the Weldon process for one ton of 35-per-cent. bleach 50 cwt. of common salt are required, according to Deacon from the pan-gas alone a ton of bleach was to be made with 32 cwt or, at the outside, with 40 cwt. of salt. There is no manganese required; the HCl is not condensed, but is employed in the state of gas as it is evolved in the decomposing-pans; the chlorine gas is at once cooled, washed, dried, and absorbed by lime. Thus at one end of the apparatus salt and sulphuric acid are introduced, and finished bleach is drawn out at the other—

* In 1880 there appear to be four or five plants at work.

unfortunately not indefinitely. Last, not least, while in Weldon's apparatus the gas has an outward pressure, which easily leads to an escape and to a nuisance, in the Deacon apparatus there is an inward suction and no escape of chlorine is possible. Deacon also asserted that so much heat was given out in the reaction that very little fuel was required for his process, as compared with Weldon's blowing-engines, pumps, agitators, &c. Everything seemed to be on Deacon's side—much larger yield, simplicity of the process, saving of labour and coals, and avoidance of nuisance. No wonder that a considerable number of English manufacturers were not frightened, even by the enormous cost of plant and the large royalty, from introducing the Deacon process. Mostly they were quite delighted with it at first. But this soon changed; and very few of them now hide their disappointment.

The following are the principal causes of the unfavourable issue of Deacon's process. The *cost of plant*, to begin with, is very high. A complete apparatus for decomposing and absorbing the gas of one sulphate-pan, working, say, 45 tons of salt per week, is at least £8000; but in some cases it has amounted to nearly twice as much. According to the most recent information, as given at the close of this chapter, which most certainly is not below the mark, each apparatus produces at most 18 to 20 tons of bleaching-powder per week; so that the interest and amortization of the above capital forms a not inconsiderable item in the cost of bleach. Also the *repairs* of such a complicated apparatus, in which a set of cast-iron pipes is continually exposed to a dark red heat, &c., must amount to a considerable figure.

Far more important, however, is another drawback, which was soon enough found out. The marbles impregnated with cupric sulphate refused everywhere to act continuously as a contact substance. After a comparatively short time the decomposition of hydrochloric acid, *i. e.* the production of chlorine, begins to decrease; and this goes on till the action ceases altogether. This sometimes happened almost directly; usually it took some time, though rarely more than four months from the time of commencement. This cessation of the action of the marbles was attributed to various causes, such as the volatilization of cupric chloride, the incrustation of the pores by ferric chloride, sulphate, soot, flue-dust, &c.; and more recently a totally different cause has been assigned for that phenomenon, as we shall see. Be this as it may,

nothing remained to be done, except stopping the work, discharging the decomposing-pans, and redipping the marbles in cupric sulphate. This cost several hundreds of pounds—that is, hardly ever less than £1 per ton of bleach made. Moreover these stoppages, amounting usually to 8–14 weeks per annum, were almost unbearable, owing to the stoppage of all other operations connected with this. The hydrochloric acid mostly had to be run away; interest and royalty were running on all the time; and much inconvenience was caused by non-fulfilment of contracts. Worst of all, the decomposer, after redipping, never worked so well as at first, sometimes not at all, whether from the pores being stopped up or from other causes; and so the work could not be carried on.

In order to remedy this defect, fatal to his process, Deacon took out a large number of patents, of which the more important shall be quoted here. On Feb. 17th, 1873, he patented the employment of a double salt of sodium and copper; on May 25th, 1875, the addition of magnesium sulphate. Neither of these had any success. On March 11th, 1875, he patented dipping in cupric chloride, or a mixture of cupric sulphate and common salt; in this case the decomposition was to take place at a much lower temperature than with cupric sulphate, less copper-salt was to be volatilized, and the process was to become more regular. Possibly this patent may work; but nothing certain can be learned about it.

According to another patent, the loss of the "catalytical force" is said to be chiefly caused by the fact that a portion of the copper-salt is volatilized, and condensed in another portion of the mass, or that the copper-salt is gradually absorbed in the interior of the mass, thus depriving the surface of its activity. To remedy this, the decomposer is now and then cooled down to 105° C., and steam admitted, which redissolves the copper-salt and spreads it more evenly over the marbles. In place of the expensive marbles burnt pyrites is to be employed, according to the patent of March 3, 1875. Recently ordinary broken bricks have been resorted to again, as we shall see.

On May 8th, 1876, Deacon patented the absorption of the hydrochloric acid escaping undecomposed out of the "decomposer," by ferric oxide dipped in a solution of cupric sulphate and piled up in upright cylinders. After the absorption has taken place, air heated to the requisite temperature, or a measure of air and hydrochloric acid, is passed through the mass charged with hydrochloric

acid, which then produces the decomposition of the hydrochloric acid. This patent has never worked in practice.

The only really successful change was this: to renounce a continuous or repeated application of the contact substance, as we shall see later on. On Jan. 28th, 1875, Deacon patented with this object an apparatus for continuously discharging the marbles. Even then, in the best case the costs for so much contact substance have to be charged to each ton of bleach made.

Since 1876 several important communications have been published upon the cause of the gradual cessation of the activity of Deacon's apparatus. Hasenclever (Deutsch. chem. Ges. Ber. ix. p. 1070) states that this takes place without any considerable loss of copper in the marbles. At the Rhenania works the decomposition of the HCl, which for some weeks had amounted to 60 per cent., suddenly fell within three days to 2 per cent. The marbles now contained upon 1·2 per cent. copper 8 per cent. $SO_3$, instead of 1·5 as required by the formula $CuSO_4$. It would thus seem that the marbles retain the sulphuric acid contained in the gases, and when they are saturated with it the decomposition ceases—possibly because the marbles are covered with a layer of sulphate, or because the $SO_3$ in contact with red-hot sulphates splits up into $SO_2$ and O, which with Cl and steam produce again $H_2O$ and HCl. Hasenclever thinks that the varying duration of the activity of the decomposers (from 1½ to 10 months) in the different works depends on the percentage of sulphuric acid in the decomposing gases. The pan-gas contains only 1·5, the roaster-gas 7·5, $SO_3$ per 100 HCl (comp. below the statements of Jurisch). In fact a works where only the pan-gas was employed, and, moreover, partly purified from sulphuric acid in a stone cistern, went on for 10 months; another, employing ordinary pan-gas, 5 or 6 months; the Rhenania works, where also the roaster-gas was employed, only 1½ month. Starting from this reasoning, Hasenclever, on Dec. 12, 1874, took out provisional protection for purifying the decomposing-gases from sulphuric acid by lime, alumina, common salt, &c., before admitting them into the decomposer—and again on June 9th, 1875, for washing out the sulphuric acid or removing it by partially condensing the gas. The latter, however, had been already patented by Deacon himself on June 1st, 1875.

Jurisch (chemist at Messrs. Muspratt's) also furnished a contribution to this question (Dingler's Journal, ccxxi. p. 356), but

subsequently had to withdraw some of his conclusions, as we shall see. He finds the principal reason why the majority of English works have given up the Deacon process in the trouble caused by the redipping of the marbles, which become the less active the oftener they are treated—also in the quick wear and tear of the whole apparatus, which renders the process more expensive than Weldon's. Whether working quickly or slowly, the general [?; comp. Hasenclever] production for 120 tons of marbles with about 1 per cent. copper is 600 tons of bleaching-powder. He finds in inactive marbles 0·92 per cent. $CuSO_4$, 5·86 $Fe_2Cl_6$, 75·30 $Fe_2(SO_4)_3$; &c. The dust accumulated between them contained 71·70 per cent. $Fe_2(SO_4)_3$; 13·64 $Fe_2O_3$, &c. The hydrochloric acid condensed in the first cooling-vessels contained per litre 329·3 gram HCl and 20·78 foreign constituents, among them 9·376 $H_2SO_4$, 0·368 $CuCl_2$, &c. Only from 15 to 25 per cent. of the copper is lost by volatilization. The cause of the loss of activity must hence be sought elsewhere; and this is done by Jurisch in the incrustration of the marbles by impurities, partly from the sulphuric acid used in decomposing, partly from the marbles themselves. Most dangerous are the sulphates of iron and aluminium; next to these, ferric chloride and arseniates. The sulphuric acid ought to be purified from arsenic, and the formation of iron and aluminium sulphates prevented, as these constitute 80 per cent. of the incrustations. The sulphuric acid found comes partly from that usually added in dipping the marbles, partly from that evaporated in the decomposing. Roaster-gas ought never to be employed, because it contains too much sulphuric acid and other impurities; of the pan-gas only the first portion, which upon 100 HCl contains from 0·251 to 1·079 $SO_3$, but later on, when the batch in the pan stiffens, as much as 8·723 $SO_3$. It is consequently best to work with two pans, each alternately sending its gas into the apparatus so long as it is still fresh and the batch thin (comp. p. 252). In order to increase the activity of the marbles on redipping, they are to be broken up and also exposed to the atmosphere in heaps for several months. The sulphuric acid is most injurious in the state of vapour, less so when it is retained by bases ($Al_2O_3$, $Fe_2O_3$) in the marbles; but when the bases are saturated the decomposition ceases. In any case most of the sulphuric acid passes through undecomposed, as is proved by its presence in the muriatic acid condensed behind the decom-

poser. Hence it is a vital question for the Deacon process, either to remove the sulphuric acid out of the gases, or to employ a large quantity of base as carrier of the active substance, *e. g.* ferric oxide as burnt pyrites [already patented by Deacon on May 3rd, 1875]. Jurisch mentions that English manufacturers had endeavoured to remove the sulphuric acid by partial condensation of the gas, but unsuccessfully, as too much HCl was condensed as well [but compare the Aussig results, Vol. II. p. 242]. Direct laboratory experiments (cited in detail) proved that the decomposition suddenly fell, on the introduction of sulphuric acid vapour, from 39·72 to 13·72 per cent. Here the incrusting action of the sulphates could not yet have come into play; and hence the action of retarding or entirely preventing the formation of Cl from HCl must belong to the sulphuric acid in the state of vapour. This conclusion was afterwards (ib. ccxxii. p. 366) entirely withdrawn by Jurisch, Hurter having proved to him the incorrectness of his experiments. Hurter states that sulphuric acid acts far less injuriously than is believed, as, similarly to arsenic and antimony, it acts by converting the copper into unchangeable compounds; the decomposition goes on *pari passu* with the volatilization of cupric chloride.

Hasenclever, in opposition to Jurisch, states (ib. p. 256) that even before the latter he had recognized the injurious action of sulphuric acid, that he had everywhere found the hydrochloric acid escaping undecomposed out of the decomposer free from sulphuric acid, and that the attempts of some English manufacturers (mentioned by Jurisch) to remove the sulphuric acid by partial condensation were only the result of an accident, without their having recognized the damage caused by that acid.

To this Jurisch replied (ib. p. 567), admitting Hasenclever's claim to priority as to the injurious action of sulphuric acid, but contesting the fact that the HCl escaping undecomposed is free from $SO_4H_2$, except for a very short time at the commencement of a period; he also cites several instances of English manufacturers introducing a partial condensation of their muriatic acid and with it a purification from sulphuric acid. Hensgen's research (cited on p. 178, Vol. II.) should also be compared here.

It is stated that Hasenclever, by some modifications of his own, hitherto kept secret, has succeeded in working the Deacon process in a satisfactory manner.

A great drawback of the Deacon process is the circumstance

that the bleaching-powder frequently comes out *too weak*. Some manufacturers have never got beyond this stage; and the majority, who at first got very good bleach, found that it gradually became weaker and weaker. Sometimes the redipping of the marbles remedied the mischief; but often it did not. The chief cause of weak bleach has been found to be the difficulty of keeping the apparatus completely tight. Just that peculiarity of the process which in some respects is one of its greatest advantages acts injuriously here, viz. the fact that in the apparatus there is a lower pressure than outside, so that no nuisance can be caused by chlorine escaping; for this facilitates the entrance of air through any leakages in the numberless joints of the iron and stoneware or glass pipes, the many-shelved absorbing-chambers, &c. Most damage is done by the entrance of fire-gases containing carbonic acid into the heating-apparatus and the decomposer, as that gas is greedily absorbed by the lime in the chambers. The influence of the foreign gases, especially $CO_2$, was minutely investigated by Hurter in the above-cited paper. In the manufacture of bleach from native manganese or by the Weldon process $CO_2$ very rarely occurs in such quantity as to prevent the manufacture of bleach containing 40 Cl per cent. But in the Deacon process it is different: for a ton of bleach 70,000 cubic feet of air are needed—that is, only about one third of the quantity required in the Weldon process; but its $CO_2$ is greatly increased on its long path through the over-heater and decomposer, where it is surrounded by fire-gases. The former is easily kept tight, but the latter only with very great care. In the construction usual till the last few years, where the decomposer consists of a square cast-iron box, the joints of the plates must open on cooling. Even if at starting a working-period all the joints have been made perfectly tight, they cannot fail to be opened by any variations of temperature during the work; for in heating up, the volume of the apparatus increases; the marbles slide down, and offer an insurmountable obstacle to the closing-up of the metal plates when they contract on cooling. With very great care an apparatus can be kept sufficiently tight for a whole year. It is never absolutely tight; but this does no harm, so long as the total surface of all the leaks together does not amount to more than 1·5 square centimetre. The situation of a leak can rarely be discovered during work; and still more rarely can it be put right without stopping the apparatus. Thus, for instance, it was found that

10,000 vols. of the gas on entering the heating-oven contained 5 vols. $CO_2$, on entering the decomposer 19 vols., on leaving the same 38·5 vols., and the bleach could not be made above 32 per cent. This source of carbonic acid, if it once exists, is the only one which is not under control. Hurter convinced himself, by direct experiments, that from a mixture of $CO_2$ and Cl calcium hydrate absorbs the former by preference, because $CO_2$ decomposes bleaching-powder; and when the top layer of lime has long ceased to absorb chlorine, it still absorbs $CO_2$. Hence in Deacon's chamber weaker bleach is always formed at the place where the gases enter, and accordingly throughout the first chamber.

Various changes in the shape of the decomposer (comp. above) have been tried for the purpose of remedying this defect; and by making the decomposer cylindrical the proportion of weak bleach is indeed much lessened. Some factories do better than others; and it is difficult to obtain altogether reliable statements upon the question.

Quite recently another source of weak bleach has been pointed out, viz. the arsenic in the sulphuric acid, both in that employed for decomposing the salt and in that employed for drying the chlorine. That arsenic exercises a disturbing influence on the activity of the copper-salt had been maintained previously (comp. p. 267); but it has been recognized latterly that the arsenious acid, or the $AsCl_3$, after the chlorine has been evolved, is oxidized very gradually, with formation of hydrochloric acid, according to the equation

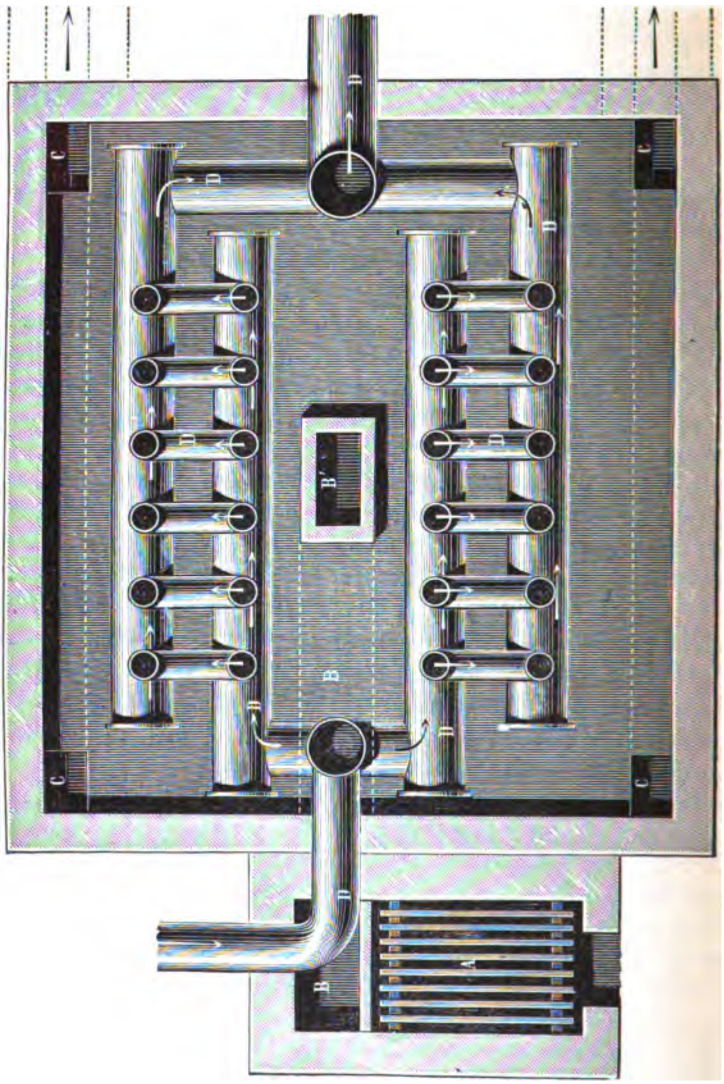
$$As_2O_3 + 2H_2O + 4Cl = As_2O_5 + 4HCl.$$

Perhaps not $AsCl_5$, but a solution of $As_2O_5$ in HCl is formed. This would appear to be very probable from a fact observed by Dr. Hewitt and Mr. Davis at the Radcliffe chemical works. There the HCl is washed out of the mixed gases by a coke-tower for strong acid and a wash-tower; the washings running off from the latter mark nothing on the hydrometer and taste hardly acid. In spite of this, in the string of pipes leading from the wash-tower to the drying-tower a solution of arsenic acid of spec. grav. 1·070 and in the pipes leading away from the drying-tower a solution of $As_2O_5$ in HCl of the consistency of treacle are condensed. It is asserted that the arsenic can be traced even to the chambers; and to this gradual formation of HCl is ascribed the largest share in the pro-

duction of weak bleach. Endeavours have been made to remedy this mischief by purifying the sulphuric acid from arsenic by heating it with common salt: the $AsCl_3$ volatilizes almost completely; and the HCl coming afterwards is nearly free from it. But this process would have to be applied not merely to the sulphuric acid of the drying-tower, but also to that employed in the decomposing-pans; and in that case it is just the strongest acid gas which could not be employed for the Deacon process. It is therefore very doubtful whether this process is economically feasible; and for the same reason the employment of sulphuric acid purified by sulphuretted hydrogen &c., or made from Sicilian brimstone, is probably out of the question. After all, it would remain to be seen whether by employing sulphuric acid free from arsenic strong bleach would be *regularly* obtained. (According to reports received in 1879, the expected success has not been obtained.)

We will conclude this chapter with communications which the author owes to a letter from Dr. Hurter (dated March 3rd, 1878), and which represent the most recent form of the process. Each individual apparatus consists of one pan (not two together) and a furnace (roaster). The gases travel separately. The whole of the pan-gas, comprising from 68 to 70 per cent of the HCl of the salt, enters the Deacon apparatus, whilst the roaster-gas passes directly to a condensing-tower. The pan-gas is cooled as much as possible by a long string of pipes and a scrubber; thus water, along with some condensed hydrochloric acid (about $\frac{1}{4}$ or $\frac{1}{5}$ of the pan-gas) is removed. The gases now enter into the *heating-apparatus*. This is a furnace 16 feet square, in which 24 vertical pipes, 12 inches wide and 9 feet high, are arranged in two sets of 12 each, so connected that as little resistance as possible is offered to the gas passing through. This arrangement will be better understood from the plan, fig. 94, which will make it clear that this heater is a close copy of the heating-stoves for the blast in pig-iron-smelting, according to the "breeches" pattern formerly in use for that purpose. A is the fireplace; B B, flue conveying the heat; B′, a chimney within the furnace, conveying the flame one foot above the bends of the heating-pipes D D; C, holes in the bed for the exit-smoke. Here the gases are heated up to 400°; the waste heat of this furnace is employed for heating the decomposer, which does not possess any fire of its own.

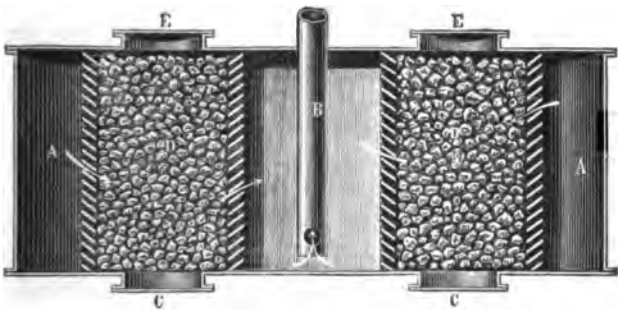
Fig. 94.



The *decomposer* is an upright cast-iron cylinder, 12 to 15 feet wide. It contains a cylindrical ring of broken bricks, supported by cast-iron shutters, as shown in the sketch section, fig. 95. The gases enter the outer ring A A, and pass radially across the

decomposing mass into the pipe B. The annular mass of active substance, D, is 3 feet thick and is divided into six compartments,

Fig. 95.




$\frac{1}{50}$

one of which is emptied every fortnight. This is done by means of the discharging-doors C C below the cylinder; fresh material is thrown in from above, through E E. This material consists of burnt clay broken up into lumps by a Carr's disintegrator, freed from dust, and dipped in a solution of cupric chloride. This mass contains about 0·6 to 0·7 per cent. of metallic copper. During the passage of the gaseous mixture, if equal volumes of air and hydrochloric acid are present, at most 50 per cent. of the HCl is decomposed. Such an apparatus furnishes, from 45 tons of salt per week, 18 to 20 tons of bleaching-powder testing 35 or 36 per cent. of available chlorine in the cask; moreover all the roaster-gas and about one sixth of the pan-gas are yielded up as strong acid even before passing through the decomposer; after that passage about one half of the undecomposed hydrochloric acid is obtained in the strong state, the remainder having a strength of about 8 or 10 per cent. By combination with a Weldon apparatus at least another 6 or 7 tons of bleaching-powder can be made from the condensed acid; so that the combined process yields 25 tons of bleach from 45 tons of salt.

After the active substance has served once, *it is thrown away.* Each hundredweight of clay produces 10 to 12 cwt. of bleach. With such apparatus no stoppages have occurred for two years. There are now at Messrs. Gaskell, Deacon and Co.'s four such and two old apparatus; and two new ones are in course of erection. The condensers, drying-towers, and bleach-chambers have not been essentially modified.

As the cylinders consist of large rings, and have only two joints exposed to the fire, there is no trouble caused by any carbonic acid; on the contrary, the process goes on without any special supervision. The alleged influence of arsenic has never been noticed there. There are now 120 tons of bleach made per week, testing 35½ per cent. of chlorine in the casks even in the heat of summer.

The considerable success attained during the last few years is stated to be chiefly owing to the recognition of the fact that catalytic actions do not go on *for ever*, and throwing away the clay taken out of the decomposer. Every thing formerly went well so long as there was a fresh filling; but when the same marbles were employed for the second or third time, mischief was done at once.

Since these statements of Dr. Hurter's are so very favourable that it can be hardly understood why, for all that, the Deacon process does not make any further progress, the author has thought it his duty to inquire into this elsewhere. From one of the few factories which alone work that process apart from the inventor's, nothing could be learned; from the other only unsatisfactory results were reported. One manufacturer, who has the greatest motive for starting the process again on the appearance of any reasonable prospect of success, having laid out £16,000 in plant for the same, but having been compelled to discontinue it, visited the works of Messrs. Gaskell, Deacon and Co. towards the end of 1878, in order to convince himself of their favourable results as described above; but his visit has not led him to recommence the manufacture of bleach by Deacon's process. Quite recently (1880) a small Deacon plant has been erected again by one of the firms previously using this process. Hasenclever's results have been mentioned already. Kunheim and Co. at Berlin are said (Chem. Industrie, 1879, p. 232) to work that process satisfactorily for chlorate of potash.

# CHAPTER VIII.

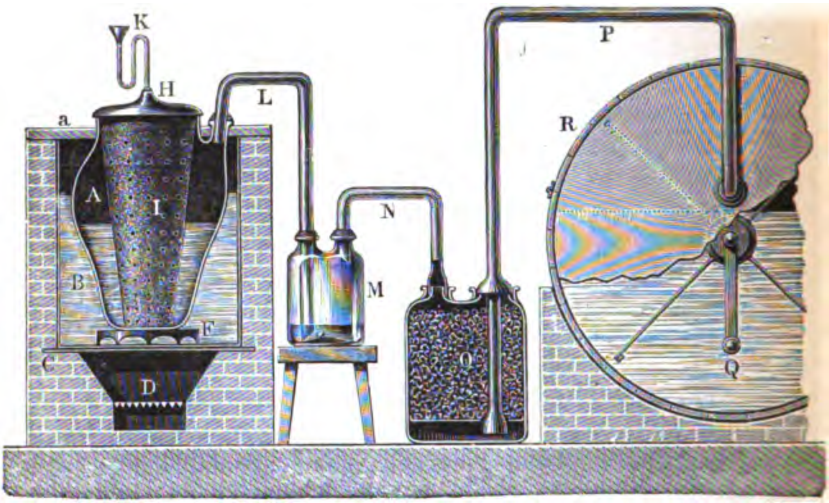
## BLEACH-LIQUORS.

Dry bleaching-powder will probably always remain that form in which the bleaching-properties of gaseous chlorine are fixed most easily and cheaply and made fit for carriage. But this advantage cannot be secured without the drawback that about one third of the lime is not converted into the bleaching-compound $CaOCl_2$. Further, bleaching-powder must be dissolved and settled before use, which is not an easy task. If, therefore, a manufacturer wishes to prepare a bleaching-compound for his own use, it is undoubtedly much better to absorb the chlorine in *milk of lime*, as in liquid bleach no excess of lime is required, and a mixture of calcium hypochlorite and chloride can be directly obtained. In this way the bleachers of Lancashire, Alsace, &c. regularly used to make their own bleach-liquor. Nowadays they do this only exceptionally; but the manufacture of *liquid chloride of lime* (*bleach-liquor*) is still a considerable industry at chemical works situated near bleach-works, where the expense of carriage is not very considerable and casks or carboys can be returned. In South Lancashire, where these conditions exist, much bleach-liquor is made—*e. g.* 5871 tons in 1866. In the north of France bleach-liquor is sent out in canal boats, made of iron and lined with a mixture of tar, pitch, and wax, constructed exactly like those for sulphuric acid, which will be described in the Appendix.

Since it is scarcely possible to construct chlorine-stills so as to sustain any considerable pressure, the chlorine in making bleach-

liquor can only come into contact with the surface of the milk of lime; but care must be taken to renew this surface continually by agitation. This is done, for instance, in Pattinson's apparatus (fig. 96). A is the chlorine-still, made of stoneware, standing on

Fig. 96.




the saucer F, in the calcium-chloride bath B; this rests on the metal plate C, and is heated by the fire in D. I is the manganese-funnel, with its cover H and the acid-pipe K (comp. fig. 60, p. 146). The chlorine passes through L into the glass wash-bottle M, partly filled with acid, from this through N into the lead vessel O, filled with lumps of manganese, and from this through P into the absorbing-vessel R. This is a horizontally placed wooden cask, lined with lead and provided with the wooden agitating-shaft Q, to which perforated gutta-percha plates are attached. The gudgeons of the shaft are made of teakwood, the bearings of ebonite. The cask is filled with milk of lime; the chlorine enters above it, but is driven into it by the agitators and is quickly absorbed. The temperature is thereby raised; and the operation must be interrupted before all the lime is dissolved, because otherwise calcium chlorate will be formed. The gas issuing from the cask, especially in the last period, is washed with water, to absorb the chlorine, before it escapes into the air. This apparatus is evidently only

adapted for small work, and is faulty in that it must be difficult to keep the ends of the shaft tight in the cask-ends. If lead pipes are employed, and if these are allowed to dip into the liquid, they are quickly acted upon, chlorine being lost, and oxygen being given off (Kunheim).

Where bleach-liquor is made on a large scale, just the same apparatus is employed as will be described in the chapter treating of chlorate of potash—that is, ordinary chlorine-stills and a connected series of upright cast-iron cylinders with vertical agitating shafts, for saturating the milk of lime. The work at first is carried on just as for chlorate. The cylinders are charged with about 1 to 1½ lb. of slaked lime per gallon of water. Care must be taken lest the chlorine be evolved too fast, which would cause too great a rise of temperature. The rule is, not to exceed 32° C.; in *no case* should 37° C. be exceeded. If the temperature should rise to this point, the gas must be stopped *at once* till the liquid has cooled down. It is very convenient to surround the absorbers with a jacket, between which and the absorber cold water is kept circulating. In any case the operation must be stopped when the specific gravity of the liquor has got up to 1·040; otherwise it will be changed into a solution of calcium chlorate. This happens sometimes after all; hence it is very convenient to combine the manufacture of chlorate with that of bleach-liquor, because then any such spoiled batches can be worked for the former. For analyses of bleach-liquor see p. 95.

An improvement in the manufacture of bleach-liquor has been proposed by Deacon (pat. Nov. 7, 1872). The slaked lime is to be replaced by calcium carbonate, in which case the reaction is

$$CaCO_3 + 4Cl + H_2O = CO_2 + 2HOCl + CaCl_2;$$

*i. e.* free hypochlorous acid is formed. This bleach-liquor may be employed directly, or converted into the ordinary kind by adding lime, which combines with the hypochlorous acid. Deacon proposes to employ the mixture of hydrated and carbonated lime which remains behind in causticizing soda; it is to be suspended in water, and treated with chlorine, like ordinary milk of lime. Or limestone or chalk in lumps may be employed, filled into a tower made of suitable material and always kept moist by water or weak bleach-liquor. This kind of operation is especially recommended for chlorine gas diluted with $CO_2$ or otherwise, *e. g.* that made by Deacon's

own process; but it has not been introduced in practice, which will be easily understood since under these conditions most of the hypochlorous acid must pass into chlorate (pp. 86 and 242).

According to Solvay (pat. Jan. 12, 1877) the calcium and magnesium silicates or aluminates, obtained by his patented process of Jan. 8th, 1877, are moistened, treated with chlorine, converted into hypochlorites, and then separated from the liberated silica and alumina by dissolving.

### *Chloride of Potash* (*Eau de Javelle*).

This liquor, first made in 1792 at the Javelle chemical works near Paris, was the first bleaching-compound known. It is made by passing chlorine gas in the cold into a solution of 1 part of potash ($K_2CO_3$) in 8 parts of water till the liquid begins to effervesce (comp. chloride of soda). Potassium chloride is separated in small crystals, together with silica (from the impurities contained in commercial potash). Since at first it was common to obtain the chloride coloured pink by the accidental presence of some salt of manganese, the consumers got accustomed to it, and this colour afterwards had to be artificially produced by adding a little still-liquor.

A very active dry bleaching compound is made by passing chlorine through a mixture of 24 parts potash with 1 part water, when a mixture of potassium chloride, hypochlorite, and carbonate is formed.

### *Chloride of Soda* (*Eau de Labarraque*).

This bleach-liquor can be made either by passing chlorine into soda or by decomposing bleaching-powder by sodium carbonate or sulphate. The original prescription, given in 1820 by Labarraque (Journ. Chim. méd. ii. p. 165), was:—Chlorine, made from 576 parts salt, 576 sulphuric acid, 448 water, and 448 manganese, is passed into a solution of 2500 parts crystallized sodium carbonate in 10,000 water. At present this liquor is made by passing chlorine into a solution of sodium carbonate in at least 10 parts of water till the liquid begins to effervesce or till it bleaches litmus. It then contains free hypochlorous acid along with sodium chloride and bicarbonate:

$$Na_2CO_3 + 2Cl + H_2O = NaCl + NaHCO_3 + HOCl.$$

If further chlorine be admitted, the bicarbonate is also decomposed with effervescence, $CO_2$ being liberated and only NaCl remaining along with hypochlorous acid :

$$NaHCO_3 + 2Cl = NaCl + CO_2 + HOCl.$$

At the same time also some chlorate is formed, especially if the specifie gravity of the liquid rises above 1·07 ; but this ought to be avoided.

If to a clear solution of bleaching-powder sodium carbonate be added, calcium carbonate is precipitated and the solution contains sodium hypochlorite and chloride. In the place of sodium carbonate, sulphate or, preferably, bicarbonate may be employed. This liquor is perfectly analogous to a solution of bleaching-powder, and quite different from that obtained by passing chlorine into soda; whilst the latter dissolves ferric hydroxide, and consequently takes away ink spots, the liquor made from bleaching-powder turns the ink spots iron-rust-coloured. The latter liquor is best prepared with sodium bicarbonate, because the precipitate settles much better than with monocarbonate. In the former case a crystalline, in the latter a pasty precipitate is formed. A slight excess of bicarbonate in the liquid is very useful for many purposes. Such a liquor is stated to bleach copper engravings in a minute without any damage to the paper, especially if the latter be at once dipped into a weak solution of sodium bisulphate(? Chem. News, xi. p. 132). A very cheap process, yielding a liquor that keeps well, is the following—passing chlorine into a mixture of milk of lime and sulphate of soda. This is the plan followed at Malétra's works at Rouen. The pharmaceutical preparation (liquor natri hypochlorosi) is obtained by shaking 20 parts bleaching-powder with 100 water, adding a solution of 25 parts soda crystals in 50 water, settling, and decanting. 1000 parts of this liquid ought to contain at least 5 parts of available chlorine.

Mayer and Schindler (Repertor. f. Pharmacie, xxxi. p. 1) obtain the compound in a solid state by passing the chlorine given off from 10 parts NaCl, 8 manganese, and 14 sulphuric acid into 19 parts of dry powdered sodium carbonate, moistened with only 1 part of water. The chlorine is slowly absorbed with evolution of heat. The product is a white powder possessing a peculiar faint smell, and is soluble in 8 parts of water.

A patent by Count Dienheim-Brochocki (No. 4483, Nov. 20,

1876) also aims at the preparation of solid bleaching-compounds. He passes cooled and dried chlorine through a solution of caustic soda or potash cooled down to 10° C., and in 24 hours obtains a crystalline product possessing extremely strong bleaching properties. By evaporating the mother liquor in a vacuum more crystals are obtained. Or chlorine is passed over a thin layer of an alkaline carbonate spread over the cooled shelves of a close apparatus; the issuing gas is passed through a very strong solution of caustic alkali. The hypochlorite obtained here is mixed with the partially saturated carbonate of the first apparatus; by this the hypochlorite is solidified, as the carbonate attracts its water of solution. In the place of that carbonate other substances having a strong affinity for water may be employed. The product is said to preserve its bleaching-properties longer than any liquid hypochlorite. It may be prepared in a granulated form by stirring the solution just before solidifying, or in the form of cakes by pouring it into a mould and causing it to solidify by the application of ice. The product is easily packed, as in the solid state it acts neither on metals nor on organic substances. This product has the advantage of being completely soluble in water, and acting very uniformly on the fibre without injuring it; its economy is more doubtful. It consists of 80 per cent. soda crystals, 8·5 NaCl, and 11·5 sodium hypochlorite. The commercial product (also known as "chlorozone" or as "essence de Boulogne") is crystalline, resembling soda, smells of chlorine, dissolves in water without residue, and is very hygroscopic; the great durability claimed by the inventor does not exist; for a sample which was kept for some time in a stoppered bottle showed only 1·33 per cent. bleaching chlorine.

Barnett and Slade (pat. Oct. 3, 1872) add to a solution of bleaching-powder sufficient solution of sodium carbonate to precipitate all the lime as carbonate, and pass carbonic acid into the decanted clear solution till all the bases are converted into bicarbonates. Thus a very efficient and yet mild bleaching and disinfecting agent is obtained.

The ordinary chloride of soda is a colourless or faint-yellow liquid, smelling like bleaching-powder and having an astringent taste. Upon vegetable colouring-matters it shows first the reaction of an alkali, and then bleaches them. On evaporation *in vacuo* needle-shaped crystals are said to be obtained, which on being redissolved in water reproduce the original bleach-liquor; but when this is

evaporated in the air, oxygen escapes and potassium chloride and a little chlorate remain behind. Acids evolve from it carbonic acid and chlorine; in the air, also, it decomposes and soda crystals are deposited.

Chloride of soda is preferred to chloride of lime in the bleaching of linen and for several other purposes.

### *Zinc Bleach-liquor.*

If a solution of zinc sulphate be added to a solution of bleaching-powder, calcium sulphate is precipitated, and the zinc hypochlorite formed at once splits up into zinc oxide and a solution of free hypochlorous acid. Zinc chloride acts similarly; for a saturated solution of zinc in strong muriatic acid decomposes as much bleaching-powder as half its weight of concentrated oil of vitriol (Varrentrapp). The reaction must be

$$CaOCl_2 + ZnCl_2 = CaCl_2 + ZnO + 2Cl.$$

Accordingly these zinc salts can be employed for liberating chlorine from bleaching-powder without the use (often objectionable) of strong acids, and thus bleaching very quickly. When this mixture is employed in bleaching paper-pulp, the precipitated calcium sulphate and zinc oxide remain in the pulp. This solution was introduced by Sacc (Wagner's Jahresb. 1859, p. 548), and has been recommended by Varrentrapp (*ib.* 1860, p. 189).

### *Alumina Bleach-liquor.*

Orioli (Wagner's Jahresb. 1860, p. 188) recommended, especially for paper-mills, a bleach-liquor made by decomposing equivalent quantities of a solution of bleaching-powder and aluminium sulphate; this had been known for many years as Wilson's bleach-liquor. Gypsum is thrown down, and aluminium hypochlorite remains dissolved. This is very unstable, and hence can be employed for bleaching without adding an acid, splitting up into aluminium chloride and active oxygen. Consequently the liquid always remains neutral, and the difficulty caused by the obstinate retention of free acid in the fibre, by which it is strongly acted upon on drying, in this case does not exist. The aluminium chloride also acts as an antiseptic, so that the paper stock can be kept for

many months without any fermentation or other decomposition. The solution is allowed to act for ten minutes in the rag-beating engine. In the case of fabrics, yarns, &c. a solution of 4 parts aluminium hypochlorite in 200 water is employed, and the stuff left in it for two or three hours. This solution can also be employed for preserving animal substances, embalming, &c., as the aluminium chloride forms very stable compounds with the albuminoid and colloid bodies and destroys the germs of putrefaction. Lastly, it is also applicable as a mordant in dyeing in lieu of aluminium acetate, as the hypochlorous acid readily escapes and the alumina remains combined with the fibre.

### *Magnesia Bleach-liquor.*

This can be made by decomposing a solution of bleaching-powder with Epsom salts and decanting from the gypsum formed. It has been proposed for bleaching by Claussen, and again by Ramsay; it is said to bleach more rapidly, and not to turn straw, flax, hemp, &c. brown, as it is free from lime; but it suffers decomposition more quickly than chloride of lime. The separated magnesia does not at all injure the fabrics (Bolley and Jokisch, Schweiz. polyt. Zeitschr. 1866, p. 120). Such a liquor was patented by Oliver, Grantham, Sinnock, and Leverson on Sept. 20, 1861, without adding any thing new. Quite recently F. Hodges has shown that a liquor of the same kind (prepared from ordinary bleaching-powder and kieserite) can bleach linen fabrics without exposure on grass, if they have previously been steeped in a hot solution of sodium carbonate.

# CHAPTER IX.

## ANALYSIS AND APPLICATIONS OF BLEACHING-COMPOUNDS.

The *technical analysis* of bleaching-powder is exclusively confined to the estimation of its percentage of available chlorine (*chlorometry*). A large number of plans have been proposed for this, the most important of which shall now be explained.

The first rational chlorometrical method was introduced, in 1835, by Gay-Lussac (Ann. Chem. Phys. [2] lx. p. 225), and is still the basis of commercial transactions in France. He availed himself of the fact that free chlorine in an acid solution oxidizes arsenious to arsenic acid:

$$As_2O_3 + 4Cl + 2H_2O = As_2O_5 + 4HCl.$$

198 parts by weight of arsenious acid are converted into arsenic acid by 142 parts of chlorine; or 1 litre of chlorine, measured at 0° C. and 760 millims mercurial pressure, weighing 3·17344 grams, oxidizes 4·425 grams $As_2O_3$. Consequently this quantity of arsenious acid is also oxidized by a certain volume of a liquid containing exactly 1 litre of chlorine. A standard solution is made by digesting 4·425 grams of pure arsenious acid with hydrochloric acid and 900 cubic centims. of water till completely dissolved, and, after cooling, diluting the solution to exactly 1 litre. Of the bleaching-powder 10 grams are weighed, triturated in a porcelain mortar with a little water to a soft mud, gradually rinsed into a litre bottle, and diluted to 1000 cub. centims. Now 10 cub. centims. of the arsenic solution are taken out with a pipette, coloured blue with a few drops

of a solution of indigo in sulphuric acid, and the bleach solution run in from a burette till the blue colour has just vanished. So long as any arsenious acid is present the chlorine is taken up by it; so that the indigo is not bleached until all the arsenic has been oxidized. The volume of bleach solution consumed corresponds to the 10 cub. centims. of chlorine required for oxidizing the 10 cub. centims. of arsenic solution employed; and the number of cub. centims. of bleach solution consumed, divided by 1000, gives the number of litres of chlorine gas which can be liberated by 1 kilogram of the bleach. This number is known as Gay-Lussac's degrees; it is used only in France; everywhere else Gay-Lussac's degrees have been abandoned along with his method. The latter is faulty, as with different degrees of dilution and different quantities of acid in excess very varying results are obtained; since chlorine and arsenious acid may coexist in dilute solutions, the bleaching of the indigo is no certain test for the oxidation of all the arsenic; and as, further, the indigo is always partially destroyed at the point where the bleach solution runs in, the colour becomes fainter and fainter, and the end of the operation is very indistinct (Mohr). All these defects have been removed by Penot's method (to be described presently); but although the latter is also due to a Frenchman, it is neither used in France nor mentioned even in the last edition of Payen's 'Précis de Chimie industrielle.'

In England, Germany, &c., the value of bleaching-powder is designated by its percentage of available chlorine. The test formerly generally employed was introduced by Graham, and improved by Otto. It is founded on the fact that ferrous salts are directly oxidized into ferric salts by bleaching-powder, and that it is easy to discover when no more ferrous salt is present. The reaction is

$$2FeO + 2Cl + H_2O = Fe_2O_3 + 2HCl.$$

For this purpose ferrous sulphate is usually employed. It is best prepared, according to Otto, in the shape of a fine powder precipitated by alcohol, which is much more slowly oxidized in the air than the ordinary crystals of copperas; but it appears then to contain less than 7 molecules of water, and consequently yields misleading results. Mohr very warmly recommended ammonio-ferrous sulphate; but this ought not to be employed, since Biltz has shown (Wagner's Jahresb. 1871, p. 255; 1874, p. 361) that a portion of the chlorine is consumed in decomposing the ammonia. The corresponding sodium compound $FeNa_2(SO_4)_2,4H_2O$ is said to

be preferable. The molecular weight of $2(FeSO_4, 7H_2O)$ is 556, and answers to $2Cl=71$; hence 0·5 gram Cl oxidizes 3·9 ferrous sulphate. This quantity is weighed off, dissolved in about 50 cub. centims. of water, and acidulated with sulphuric acid. Further, exactly 5 grams of the bleaching-powder to be tested are weighed off, most carefully triturated with water to a thin paste, and rinsed into a measuring-tube divided into 100 equal parts, *e.g.* ½ cub. centim. each. The burette is filled up to the mark with the rinsings, and its contents well mixed up. This bleach-solution (which ought to have the appearance of milk and not show any small lumps) is poured with constant agitation into the iron-solution prepared before; and from time to time the mixture is tested for unoxidized iron by taking out a drop with a glass rod and putting it beside one of a solution of potassium ferricyanide quite free from ferrocyanide. When no more blue precipitate, but only a brown coloration ensues, the operation is finished. Thus just as much bleach has been consumed as corresponds to 0·5 gram of chlorine; hence the percentage of available chlorine in the bleach is found by dividing $100 \times 10 = 1000$ by the number of measures of bleach-solution (made from 5 grams) consumed. Thus, if 29·5 measures have been consumed, the bleach holds $\frac{1000}{29 \cdot 5} = 33 \cdot 5$ per cent. of available chlorine.

Graham and Otto's process cannot be recommended at all. It requires exact weighings of bleaching-powder and iron salt for every single test. It is not easy to make from 5 grams of bleach, with all rinsings, a measure of 50 cub. centims. really free from small lumps; the burette must be often shaken to keep the liquid in the same state. When the proper point has been exceeded, correction is impossible, and a new test must be made. Lastly, the accuracy of the test entirely depends upon the absolute purity of the iron-salt employed, unless the very tedious plan is adopted of dissolving pure iron wire for each test. Hence the process is much more troublesome and tedious even in manipulation, and requires more practice, than the iodine method or Penot's arsenic method. And, after all, it is decidedly inaccurate; for with the best stirring it is impossible to prevent an escape of chlorine when the bleach-solution is being poured into the acid liquid: the results obtained are always too low, and that by 1 or 2 per cent. Another source of error is, that any chlorate present acts, even when cold, upon ferrous sulphate

in an acid solution, as was shown by Wright (Chem. News. xvi. p. 171); the same perhaps holds good of Wagner's test, in which also an acid solution is employed, whilst Penot's test, in an alkaline solution, is not at all influenced by the presence of chlorates.

Another, much more trustworthy method is the iodine method, indicated by Bunsen and improved by Wagner, who substituted for the solution of sulphurous acid one of sodium hyposulphite. It utilizes the fact that bleaching-powder liberates from a potassium-iodide solution in the presence of free hydrochloric acid a quantity of iodine equivalent to the available chlorine, the iodine remaining dissolved in the excess of potassium iodide. On addition of sodium hyposulphite, tetrathionate is formed, according to the equation

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI;$$

so that, after the iodine has been completely used up, the liquid, previously dark brown or coloured blue by starch, is decolorized. 10 grams of bleaching-powder are ground up with water, diluted to one litre; 100 cub. centims. (=1 gram of bleach) are taken out, and to these are added 25 cub. centims. of a 10-per-cent. solution of potassium iodide and hydrochloric acid till the reaction is acid. To this brown liquid the operator adds decinormal hyposulphite solution (containing 24·8 grams of that salt per litre) from a burette, at the same time stirring. The brown liquid gradually turns lighter, and at last becomes colourless, completing the operation. The transition is quite sharp and unmistakable. The number of cub. centims. of hyposulphite consumed, multiplied by 0·355, shows the percentage of available chlorine in the bleaching-powder. (Some precautions to be used in testing with hyposulphite have been mentioned above, p. 124.) Wagner's process is very convenient and quickly executed; and in the absence of chlorate it is also very exact; but in the presence of that salt it is inaccurate, unless the slightest excess of HCl be avoided, which is a very difficult matter. Chlorate acts equally upon KI in the presence of HCl; but its chlorine is useless to the consumer. This assertion (made by Mohr) is denied by Wagner himself, and has also been disproved by Winkler (Dingl. Journ. cxcviii. p. 143). The process is also somewhat expensive as an every-day test, on account of the potassium iodide. Wagner's proposal to employ the decolorized solutions over again for dissolving iodine is not feasible, on account

of the dilution; and Mohr asserts that it is inaccurate in the presence of alkaline carbonates.

The process which has recently been employed in most laboratories (elsewhere than in France) is titration with an alkaline arsenite-solution (while Gay-Lussac had employed an acid solution). This process fully deserves the preference given to it, on account of its being entirely free from sources of error, and its great simplicity and facility of execution. The reaction is the same as in Gay-Lussac's process; but by employing an alkaline liquid any escape of chlorine is avoided; and the indicator, iodized starch-paper, has none of the drawbacks attaching to the indigo-solution.

A standard solution is made by dissolving $\frac{1}{40}$ molecule $=4{\cdot}95$ grams of pure powdered arsenious acid in four times its weight of pure sodium carbonate or bicarbonate and about 200 grams of boiling water. Neither the arsenic nor the soda must contain any oxidizable sulphur compounds; otherwise the solution will not keep. Hence it is safest to employ sodium bicarbonate, which is always pure in this respect, and to test the arsenious acid (of which the porcelain-like pieces occurring in commerce are usually quite pure) by incipient sublimation between two watch-glasses; the red arsenic sulphide, subliming first, is easily recognized. A small sample, heated on platinum foil, should be completely volatilized. The arsenious acid has the convenient property of not being hygroscopic, and hence is easily weighed with accuracy. When it has been completely dissolved, the liquid is diluted to a litre; it keeps wholly unchanged for years, even in bottles not quite full. The test-paper is made by boiling starch for some time with one hundred times its weight of water, filtering, adding a little pure potassium iodide, and soaking Swedish filtering-paper in the liquid. The paper acts best when made freshly every time by means of a starch-solution, rendered durable by the addition of common salt, zinc chloride, or any other known means. Such paper is spread out on a porcelain slab (or large crucible-cover); it is much more sensitive than dried paper; and it can be used over and over again, if kept in a place free from dust, as the iodine spots made upon it bleach out after a few hours, and the paper is always ready for use again after moistening.

For carrying out the operation, a bleaching-powder solution is made just as described above, viz. by grinding the powder with a

little water in a small mortar with its spout greased, diluting with more water, rinsing out, &c. Sometimes warm water is used; but this should be done cautiously, as such solutions of bleach quickly spoil. The author weighs each time 7·100 grams of bleach, which is made up to a litre; for each operation 50 cub. centims. (=0·355 gram) are taken. This, if it contained 100 per cent. Cl, would require 100 cub. centims. of the $\frac{1}{40}$ molecular arsenic-solution; hence the number of cub. centims. of the arsenic-solution actually used shows without any calculation how much per cent. of available chlorine is present in the bleaching-powder. The testing is performed thus:—The 50 cub. centims. of bleach-solution are pipetted into a beaker, which is agitated while not quite so much arsenic-solution as is thought necessary is poured in from a pinchcock burette; a drop of the mixture is put on the damp potassium-iodide starch-paper. According to the depth of colour (which with a very large excess of chlorine is not blue, but brown), more or less arsenic is poured in again, and again tested, till at last no spot is produced on the test-paper. With a little practice, only four or five testings need be made in order to titrate down to $\frac{1}{10}$ or even $\frac{1}{20}$ per cent.

Mohr adds at once an excess of arsenic-solution, then a little starch-solution, and titrates back with a solution of iodine equivalent to the arsenic-solution (containing 12·70 grams of iodine and about 25 grams of KI per litre). Thus the testing of spots is saved; but two standard liquids are required instead of one, and the iodine-liquid cannot be employed even in a pinchcock burette. Hence Penot's original process is more usually employed in factories.

A cross between Gay-Lussac's and Penot's process is that of Davis (Chem. News, xxvi. p. 25). He dissolves 13·95 of pure $As_2O_3$ by heating in 40 cub. centims. of pure glycerine, dilutes to 1 litre, and takes 10 cub. centims. of this for each test; this is coloured by a drop of indigo-solution, and a solution of 5 grams of bleaching-powder in 250 cub. centims. water poured in from a Gay-Lussac burette till the blue colour of the liquid has turned brownish yellow. The number of cubic centims. consumed is divided by 500 to find the percentage of the bleach. This process has the advantage over Gay-Lussac's in that it does not work in the presence of hydrochloric acid, by which chlorine is sometimes lost. If Davis calls this "a puerile objection," this expression turns against him-

self. But the small advantage of having the indicator in the liquid itself is obtained by a considerable sacrifice of sharpness, as has been shown above (p. 284); and even this small advantage is shared by Penot's process as modified by Mohr, while it is far more than outweighed by the great inconvenience that in Davis's process not the standard solution, but the bleach-solution is poured in from the burette, and that pinchcock burettes cannot be employed.

The process of Herreshoff (Chem. News, xxiii. p. 293) is founded on the application of stannous chloride and retitration by potassium bichromate, iodized starch being the indicator. It is much more troublesome than Penot's process. Quite useless are such proposals as that of Schmidt and Bennewitz (Journ. prakt. Chem. [2] viii. p. 3) to employ the hydrochlorate of orthoamidophenol, which is to be converted quantitatively into orthodichlorazophenol. The correctness of this process has been tested by Penot's method!

Older, but useless, or now disused, chlorometrical methods were:—those of Welter and Decroizilles with standard sulphindigotic acid; Noellner's gravimetrical test, viz. heating with sodium hyposulphite, decomposing with HCl, and estimating the sulphuric acid formed; Bunge's process of converting ferrous chloride into ferric chloride, reconverting into ferrous chloride by a strip of copper, and estimating the loss of weight of the latter; Gay-Lussac's with potassium ferrocyanide, and indigo-solution as indicator; Balland de Toul's and Marezeau's by mercurous nitrate; Henry and Plisson's by decomposing ammonia and measuring the nitrogen; Fordos and Gélis's direct titration with sodium hyposulphite.

In all prescriptions for testing bleaching-powder stress is laid upon employing, not a clear, but a turbid, shaken-up solution of bleach for titrating. The reason is because the bleaching chlorine is never all dissolved, but a portion of it remains in the sediment, and hence less is always found on titrating the clear solution than with the turbid liquid. But undoubtedly this custom is not altogether justifiable; for the consumers must nearly always use for their purposes, not the turbid liquid, but only a clear solution. This would not matter very much, if the proportion of available chlorine in the liquid to that in the sediment were always the same; but while there are no experiments extant upon this point such constancy of proportion is not likely to exist, since on dissolving some descriptions of bleach they behave very differently from others,

according to the nature of the lime. A general agreement to titrate only the clear solution, and to abate accordingly the requirement of 35 per cent., would be much more rational.

The following table (calculated by Pattinson, Chem. News, xix. p. 111) shows the proportion between the Gay-Lussac degrees, used in France, and the percentage of available chlorine as designated in England, Germany, &c., on the assumption of 35·46 for the molecular weight of chlorine, 0·08961 gram for the weight of 1 litre of hydrogen at 0° and 760 millims. pressure, and, correspondingly, 3·17763 grams for 1 litre of chlorine gas.

| French degrees. | Per cent. Chlorine. | French degrees. | Per cent. Chlorine. | French degrees. | Per cent. Chlorine. |
|---|---|---|---|---|---|
| 63 ......... | 20·02 | 85......... | 27·01 | 107......... | 34·00 |
| 64 ......... | 20·34 | 86......... | 27·33 | 108......... | 34·32 |
| 65 ......... | 20·65 | 87......... | 27·65 | 109......... | 34·64 |
| 66 ......... | 20·97 | 88......... | 27·96 | 110......... | 34·95 |
| 67 ......... | 21.29 | 89......... | 28·28 | 111......... | 35·27 |
| 68 ......... | 21·61 | 90......... | 28·60 | 112......... | 35·59 |
| 69 ......... | 21·93 | 91......... | 28·92 | 113......... | 35·91 |
| 70 ......... | 22.24 | 92......... | 29·23 | 114......... | 36·22 |
| 71 ......... | 22·56 | 93......... | 29·55 | 115......... | 36·54 |
| 72 ......... | 22·88 | 94......... | 29·87 | 116......... | 36·86 |
| 73 ......... | 23·20 | 95......... | 30·19 | 117......... | 37·18 |
| 74 ......... | 23·51 | 96......... | 30·51 | 118......... | 37·50 |
| 75 ......... | 23.83 | 97......... | 30·82 | 119......... | 37·81 |
| 76 ......... | 24·15 | 98......... | 31·14 | 120......... | 38·13 |
| 77 ......... | 24·47 | 99......... | 31·46 | 121......... | 38·45 |
| 78 ......... | 24·79 | 100......... | 31·78 | 122......... | 38·77 |
| 79 ......... | 25·10 | 101......... | 32·09 | 123......... | 39·08 |
| 80 ......... | 25·42 | 102......... | 32·41 | 124......... | 39·40 |
| 81 ......... | 25·74 | 103......... | 32·73 | 125......... | 39·72 |
| 82 ......... | 26·06 | 104......... | 33·05 | 126......... | 40·04 |
| 83 ......... | 26·37 | 105......... | 33·36 | 127......... | 40·36 |
| 84 ......... | 26·69 | 106......... | 33·68 | 128......... | 40·67 |

*Applications of Bleaching-powder and other Bleaching-compounds.*

Bleaching-powder is mostly employed for bleaching cotton, flax, hemp, materials for paper-making, &c.; next to this, it is most frequently used for disinfecting and sanitary purposes in general. It is also used in the preparation of chloroform, as an oxidizing agent in the manufacture of colouring-matters and other chemicals, in dyeing and calico-printing (especially as a "discharge"), and in very many other cases where its oxidizing and bleaching properties come into play, for making oxygen with the assistance of cobalt-salts, for purifying spirit of wine from fusel oil, &c.

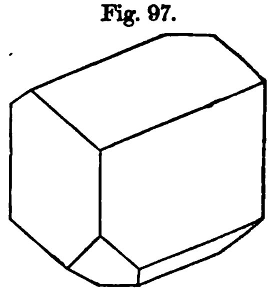
The *statistics* of the production of bleaching-powder have been combined with those of alkali (p. 67 *et seq.*). We will here only point out the remarkable fact that during the last ten years (that is, since and, for the most part, through the introduction of the Weldon process) the production of bleaching-powder in England (altogether predominant in its manufacture) has risen from 50,000 tons to far above 100,000 tons per annum.

# CHAPTER X.

## CHLORATE OF POTASH.

POTASSIUM chlorate, according to Kopp's Gesch. der Chemie, iii. p. 362, seems to have been prepared already in the 17th century, as is proved by two passages in Glauber's writings; but its nature was not recognized, Glauber taking it for saltpetre. Its real discovery and investigation are due to Berthollet, 1786–88. Gay-Lussac, Graham, and others gave prescriptions for its preparation; but only that of Liebig made its manufacture on a large scale economically possible. Since then this salt has entered into the cycle of alkali-making, because its manufacture, like that of bleaching-powder, is only possible in connexion with the preparation of sulphate from common salt and sulphuric acid. Certainly much fewer works make chlorate than bleach; the former belongs to the finer chemicals, which as a rule leave a larger margin of profit than articles made in large quantities but which are only saleable to a restricted extent and can only be made with much more trouble and care. It is, for instance, a condition in trade that chlorate of potash should not contain more than 0·05 per cent. chlorine as chlorides, or should consist of 99·9 per cent. chemically pure $KClO_3$.

Fig. 97.



Potassium chlorate forms transparent brilliant crystals of the monoclinic system (fig. 97). The two prevailing prisms form apparent rhombohedra. Large crystals are rarely found; the salt, as sold, is in small iridescent laminæ and plates. When crystallizing from liquors containing very

much calcium chloride (as in the crude crystals made at the factories) it shows an entirely different habit, viz. small, pointed, needle-shaped crystals.

It is softer than rock-salt; its specific gravity is 2·326–2·35. It does not change in the air, has a cooling, astringent, and nitre-like taste. Its chemical composition is :—

| | | |
|---|---|---|
| K | 39·13 = | 31·92 per cent. |
| Cl | 35·46 = | 28·92 „ |
| 3O | 48 = | 39·16 „ |
| $KClO_3$ | = 122·59 | 100·00 |

Potassium chlorate, according to Pohl (Liebig's Jahresb. 1851, p. 59), fuses at 334° C. without losing oxygen; but it decomposes at 352° with effervescence, more rapidly at a red heat, partly splitting up into potassium chloride and oxygen, and partly, unless the heat is too high, into potassium chloride and perchlorate; on further heating the latter also splits up into KCl and O. According to Carnelly (Chem. Soc. Journ. 1878, ii. p. 277), its fusing-point is 359° C.; the temperature at which it begins to decompose must be a little higher.

Potassium chlorate is soluble in water, heat being absorbed. According to Gay-Lussac, 100 parts of water dissolve

| At 0° | 13°·32 | 15°·37 | 24°·43 | 35°·02 | 49°·08 | 74°·89 | 104°·78 |
|---|---|---|---|---|---|---|---|
| 3·33 | 5·60 | 6·03 | 8·44 | 12·05 | 18·96 | 35·40 | 60·24 pts. by weight. |

According to Girardin,

| At 28° | 35° | 40° | 47° | 65° |
|---|---|---|---|---|
| 9·5 | 12·3 | 14·4 | 18·3 | 29·1 parts by weight. |

Accordingly its solubility increases, especially above 50°, at a much higher rate than the temperature. The saturated solution boils at 105° (Kremers). Specific gravity of the solution at 19°·5 (experiments by Kremers, calculated by Gerlach) —

| Per cent. $KClO_3$... | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. |
|---|---|---|---|---|---|---|---|---|---|---|
| Sp. gr. ............ | 1·007 | 1·014 | 1·020 | 1·026 | 1·033 | 1·039 | 1·045 | 1·052 | 1·059 | 1·066 |

In absolute alcohol it is insoluble, in spirit of wine very little soluble, and the less so the stronger the spirit.

For the *preparation* of potassium chlorate several plans have been indicated.

1. That of Gay-Lussac. A solution of one part of potassium hydrate in 3 parts of water is completely saturated with chlorine gas, allowed to stand for a few days, and then heated to ebullition, so as to decompose the hypochlorite:

$$6KOH+6Cl=5KCl+KClO_3+3H_2O.$$

According to Morin (Ann. Chem. Phys. xxxvii. p. 154), only 1 equivalent of potassium chlorate to 18 of chloride is obtained, because on evaporating the solution much oxygen escapes. Instead of caustic potash a solution of potassium carbonate may be saturated with chlorine gas; but this is much more difficult, and causes much loss of chlorine and hypochlorous acid, for which reason caustic potash is preferable. In either case a very large quantity of potassium hydrate or carbonate is converted into the much less valuable chloride, which is also very difficult to separate from chlorate; and hence this process does not possess any technical interest.

2. Graham (Phil. Mag. xviii. p. 518) proposed to save potash by saturating an intimate mixture of 1 equivalent of potassium carbonate and 1 of dry calcium hydrate (*i. e.* 100 $K_2CO_3$ + the hydrate from 40 CaO) with chlorine. The absorption takes place quickly, the temperature rising to 100° C. and the water being evaporated. The saturated mass is heated in order to decompose all hypochlorite, and extracted with water; potassium chlorate and chloride are dissolved, and calcium carbonate remains behind. This process is also not applicable in industry, compared with Liebig's; neither is this the case with a proposal made by Crace Calvert as late as 1850, for passing chlorine into a heated mixture of caustic-potash liquor and lime (Chem. Soc. Quart. Journ. iii. p. 106).

3. From bleaching-powder, Liebig proposed (Mag. Pharm. xxxv. p. 225) to grind up 10 parts of ordinary bleaching-powder with water, and evaporate to dryness. Thus a mixture of calcium chlorate and chloride is formed, which is dissolved in water, filtered and mixed with 1 part of potassium chloride, and evaporated to dryness. But in this case there is a considerable loss by evolution of oxygen in evaporating (comp. p. 88).

4. The only technically available process was also indicated by Liebig (Ann. Pharm. xli. p. 307). His prescription is to make 1 molecule of potassium chloride and 3 of quicklime into a thin paste with water, to saturate this with chlorine, filter, and to obtain from

the solution, which contains only potassium chlorate and calcium chloride, the former by crystallization. The process now employed on the large scale differs from this only in the potassium chloride being added at a later stage, frequently only after completely saturating the lime with chlorine. We will describe this process in detail.

The generation of the chlorine takes place exactly as described for bleaching-powder; nor need the stills be constructed for any stronger pressure than usual (*i. e.* about 4 inches water-pressure), as the absorption by the milk of lime does not take place under pressure. The *absorbing-apparatus* must, however, be arranged so that the surface of the liquids, upon which alone the gas can act, is constantly renewed. For this purpose it is necessary to cause the liquid not merely to revolve, but to splash about violently. Under such circumstances the gas is absorbed quickly, and with considerable evolution of heat, so that artificial heating of the liquid is not required.

The author once found, in a factory which no longer exists, a very crude kind of absorption-apparatus. A square stone cistern like a deep chlorine-still was filled with milk of lime, which was continually running out at the bottom, and constantly baled back again, by a workman, into a funnel at the top. The chlorine gas was also introduced at the top by a rose, and caused a suffocating stench whenever the man ceased for a moment—although the unabsorbed gas did not escape directly into the air, but into two small bleaching-powder chambers, the contents of which were used the next time in lieu of fresh lime.

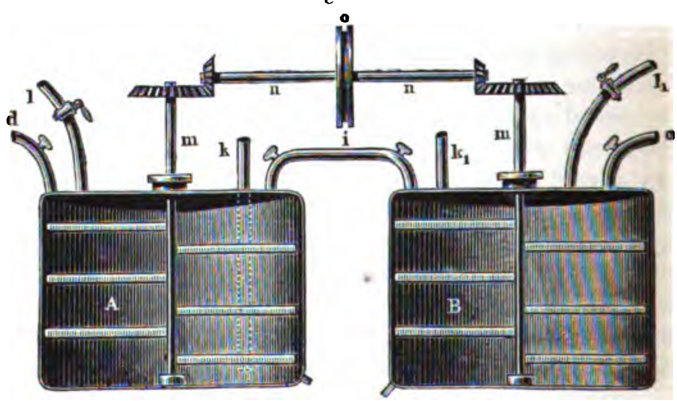
Mechanical agitation is far preferable. With this, two cisterns, at least, are employed, and are alternately the first and the last in regard to the entrance of the gas. The following is a description of a comparatively small apparatus of this kind. The still-gas passed through the vessels represented in fig. 98. The lead gas-pipe *x* divides into two branches, each of which enters a lead cylinder of 12 inches height (I & II) and descends nearly to its bottom. These cylinders can be filled with water through the funnels *e* and *f*, and emptied by taking out the plugs *g* and *h*. This contrivance serves for allowing the gas to come out either at *d* or at *c*, and consequently to pass into either one or the other absorbing-cistern. In the case sketched in the figure the gas from *x* can only get into I through *a* and pass on through *c*, because *b*

is luted. But when it has to pass through II and *d*, II is emptied by taking out *g*, and I filled through *f*.

Fig. 98.


The absorbers themselves (shown in fig. 99) are cylinders made of strong lead, A and B, about 2½ feet wide and 2 feet high; *c* and *d* are pipes for chlorine gas (compare fig. 98); *i*, communication for gas between A and B; *k* and $k_1$, escape-pipes with water-

Fig. 99.




lutes (not shown); *l* and $l_1$, steam-pipes; *m* and *m*, iron agitators covered with lead, set in motion by the shaft *n*, on which the pulley *o* was fixed. From *o* an endless cord passed over another pulley,

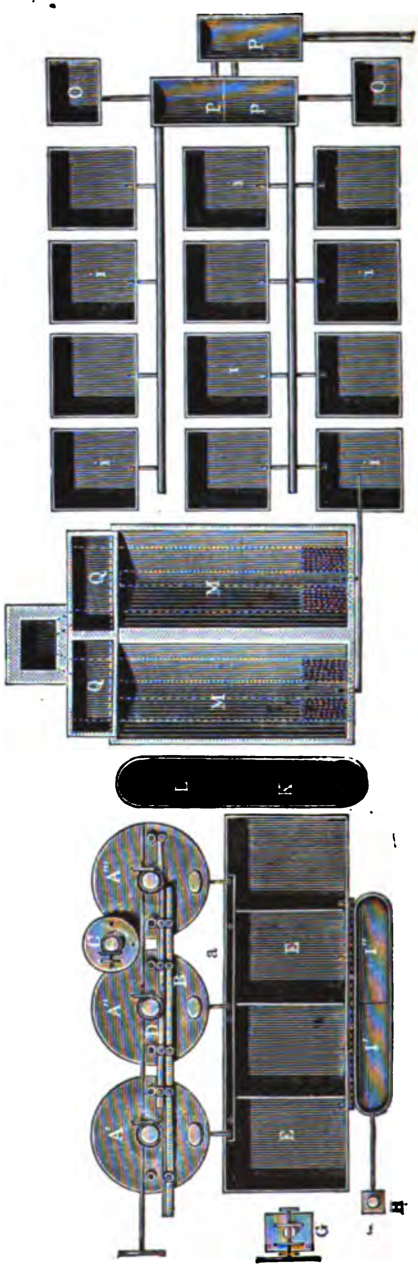
which was turned round by a boy by means of a crank. The working taking takes place as follows. If the gas enters B through *c*, that which is not absorbed here passes on through *i* into A, and is there completely absorbed by fresh milk of lime, so that next to no chlorine gas escapes through *k* into the chimney. The steam from $l$ and $l_1$ serves only to start the process. When the lime in B has become saturated, the course of the gas is changed, and the contents of B are taken out, and replaced by fresh milk of lime. The gas now enters through *d* into the half-saturated contents of A, then through *i* into B, and through $k_1$ into the chimney. The work goes on very smoothly and simply.

Endeavours (*e. g.* by J. Young) to introduce agitating-apparatus of other constructions than the ordinary cylindrical ones have not been successful. Neither is the patent of Hunt (July 21, 1871) carried out, according to which dilute chlorine gas is to ascend in a shaft filled with bricks and in which milk of lime or a milk of lime and potassium chloride runs down (that is, just as in Weldon's magnesia-process, p. 241).

The following is a description of an apparatus employed for the production of chlorate of potash on the large scale. Figs. 100 and 101 show the apparatus for manufacturing the crude salt. The dimensions as given below suffice for making 7 or 8 cwt. of chlorate in 24 hours; but more cylinders may be combined together, and a correspondingly larger production obtained. A′ A″ A‴ are the absorbing-cylinders (these are called "octagons" in Lancashire, from the shape of the stone cisterns formerly employed); B is the main gas-pipe, C the reserve absorber, D the return gas-pipe; E E are the settlers for the calcium chlorate; G is the steam-engine, H a pump for the chlorate liquor from the well I, K a tank for concentrated chlorate liquor, L another for washings; M M, boiling-down pans for chlorate liquor; *i i*, crystallizing-vessels for crude salt; O O, drainers for the same; P P, catch-wells for any salt carried away on running-off the mother-liquors; Q, a pan (heated by the waste heat of the pans M M) for dissolving any crusts and mud of chlorate and running this solution straight into the pans M M.

The *absorbers* A′ A″ A‴ are made of cast iron, since it has been ascertained that the former stone "octagons" are quite uncalled-for; even stone covers have been mostly abandoned. The details

Fig. 100.



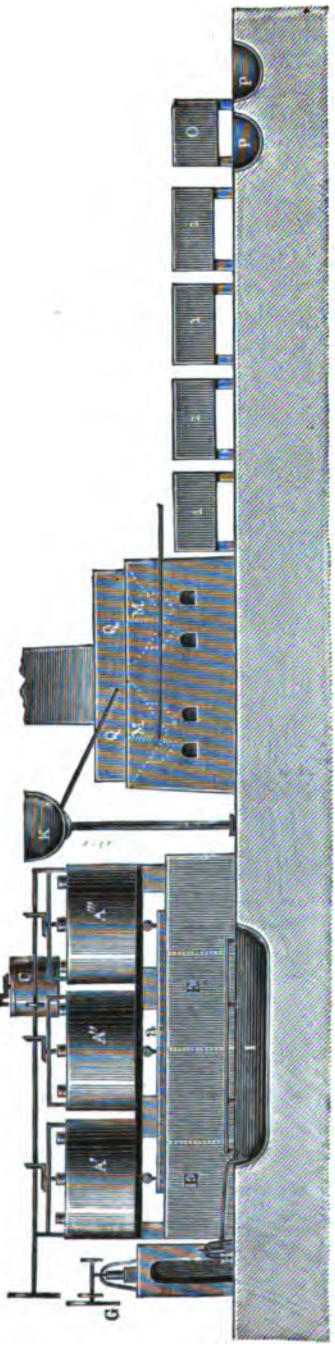
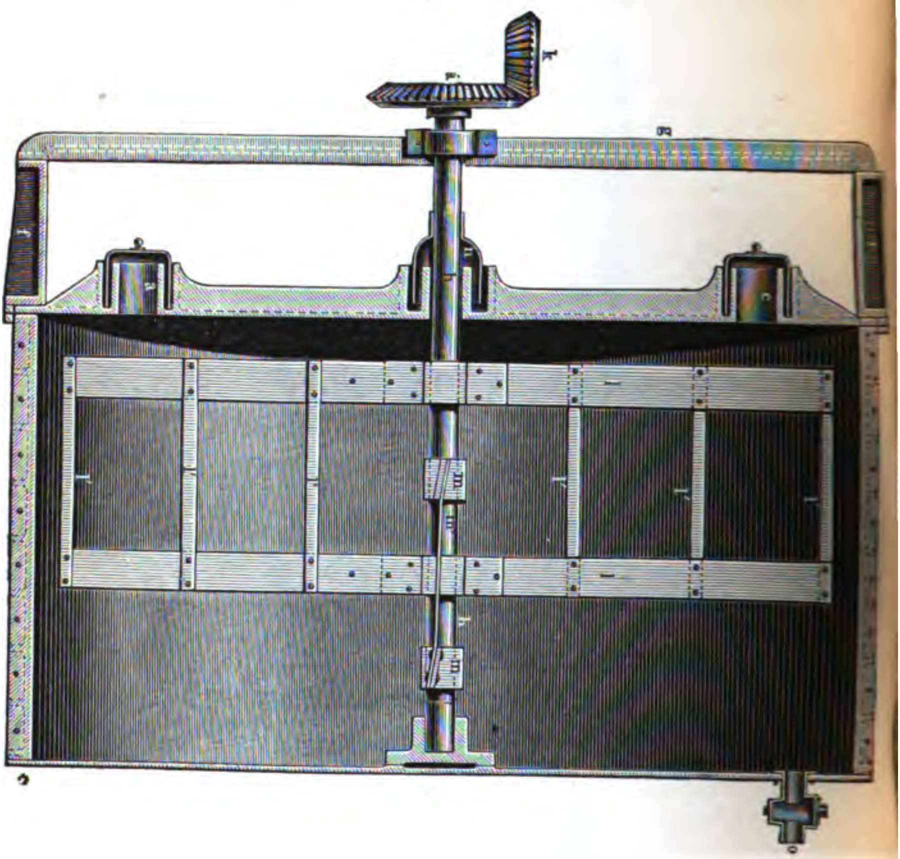


Fig. 101.

of their construction can be seen from fig. 102 (sectional elevation) and fig. 103 (top view). They are 10 feet wide and 5 ft. 6 in.

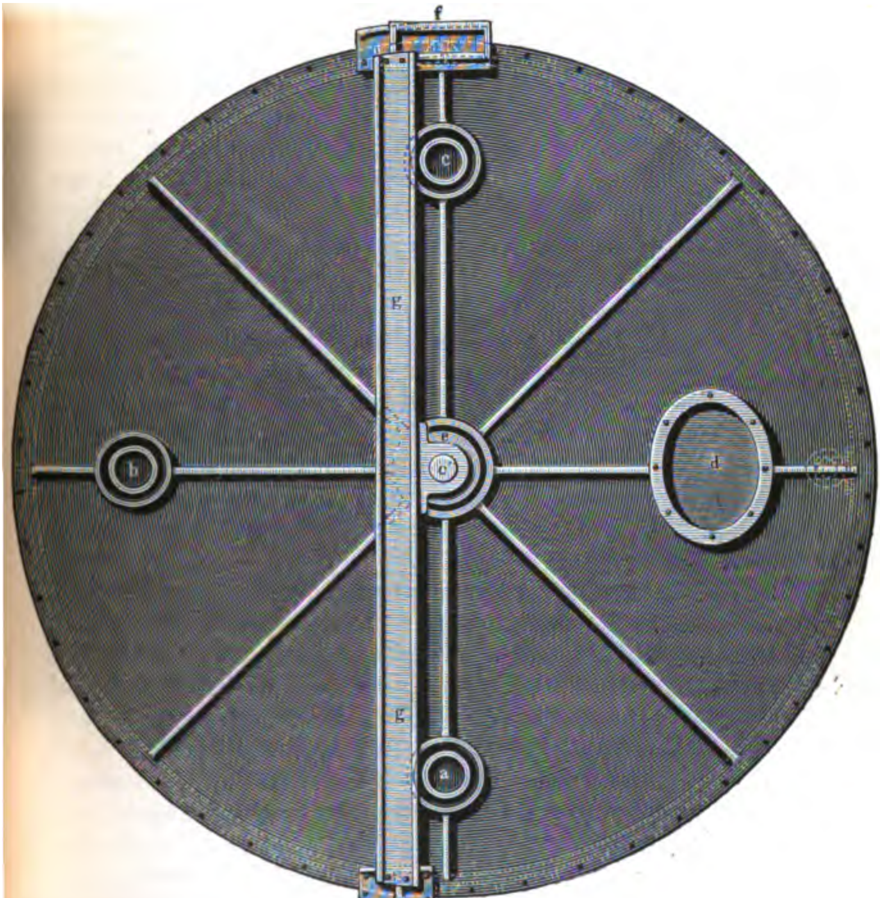
Fig. 102.



high; the bottom and top are each made in one piece, the shell in segments; all joints are made with flanges and screwbolts and rust-cement. The thickness is only one inch; but the flanges are strengthened in the usual way; and so is the top by six radial ribs. There are three 6-inch openings in the top (*a*, *b*, *c*), for introducing and taking away the chlorine; another, *d*, is for the man-hole, *e*

for the central agitating shaft. *a, b, c,* and *e* are each fitted with two concentric, upright, cast-iron flanges, forming a 6-inch water lute. When no gas-pipe is connected with them, *a, b,* and *c* are closed by caps of cast-iron, earthenware, &c. . The oval man-hole

Fig. 103.




*d* (18 × 15 in.) is fitted with an inner margin of strong sheet-lead reaching 6 or 8 inches downwards and forming a water lute when the cylinder is filled; apart from this the man-hole is always open, so that observations can be made at any time, samples drawn, and

hydrate of lime put in. The central opening, *e*, also forms a water lute; in this the shaft *h* rotates gas-tight without any stuffing-box, by means of a cup *n* fastened to it. The shaft *h* is made of wrought iron, 4 inches square, turned round in the gudgeons; it is guided by two castings (*f f*) bolted to the top flanges, and a cross bar *g*, to one side of which a bearing *e'* is cast; at the bottom the shaft *h* rotates in a footstep. It is set in motion by conical wheels *i* and *k* (2 feet and 1 foot). *k* is attached to a 3-inch shaft, which passes over all the cylinders, by means of a friction-clutch. A two-horse power steam-engine can drive six such agitators. The shaft *h* carries inside the agitating-arms *l l* and *m m*, the former at right angles to the latter; they are made a little slanting, to cut better through the liquid. Each two of them are connected by the cross arms *l'* and *m'*; fig. 102*a* shows a horizontal section of the main shaft, with the arms attached. In the bottom there is a cast-iron 3-inch or 4-inch discharge-cock *o*.

Such large cylinders are only adapted for a manufacture on a somewhat considerable scale. Smaller cylinders are usually found at continental works (say 6 feet in diameter and 3 feet high). They do not, however, seem to work so well as the large ones; for instance, they do not get hot enough without introducing steam, which, again, dilutes the liquid. Small cylinders should have a non-conducting jacket, while in large cylinders such jackets would cause overheating.

Three or more cylinders form a set, which always work together. By means of the 5-inch lead or earthenware pipes C, the chlorine can be sent at will into each of the cylinders,—*e. g.* A' (fig. 100), by its left-handed water-lute *a*, which corresponds to the water-lute *a'* on the pipe B; *a* and *a'* must be joined by a movable double elbow-pipe, or, still better, by the contrivances represented on figs. 54 to 56, p. 141. The gas issues from *c* (*d* only serves in special cases), and passes through a special pipe into the opening *a* of the next cylinder A''; from this the gas passes from *c* to *a* in A''', and from this at last by *c* to the small reserve cylinder, C, which is also fitted with an agitator, and which stands high enough for its liquor to run into the man-holes of the cylinders A', A'', and A'''. When A' is finished, the fresh gas is admitted into A'', and A' charged anew; the gas from A''' is then taken back to A' by the 4-inch connexion-pipe D. The cylinders now work in the order A'', A''', A'; from A' the gas again passes by a 4-inch lead pipe to C. It is obvious

that the work goes on all the more smoothly and well the more cylinders work together; six is a very good number. In this case the chlorine is absorbed almost entirely before it arrives in C; but, for the sake of safety, C should be connected with a small bleaching-powder chamber to absorb any gas escaping from the apparatus in consequence of an accidental stoppage of the machinery, too violent an evolution in the stills, &c. The bleach made there is not very well adapted for a commercial article, but is used in the agitators in the place of fresh lime. Where bleaching-powder is manufactured along with chlorate, a branch from the main gas-pipe should go direct to the powder-chambers, to take the gas directly there during any stoppage in the chlorate department.

The absorbers are filled up to 10 inches below their top with water or weak liquors (washings from the mud of former operations); they should not be filled any higher, because the lime takes some space, and the bulk of the liquid is expanded by the heat and by the water condensing from the chlorine; some space must always remain for the gas. The quantity of the lime must be in a certain proportion to that of the water, so that the calcium chlorate liquor resulting from it may not show more than 24° to 26° Tw. (measured cold). When too much lime is taken, stronger liquor results, which takes a disproportionately long time for finishing. For each cylinder of the size shown 35 cwt. of hydrated lime are required, which should be thrown through a half-inch sieve. On the first day only 23 cwt., and the next day 12 cwt. of the above quantity are charged; on the third day usually the whole contents of the cylinder are changed into chlorate.

In the regular course of working, the cylinder just charged with lime receives gas at first from an older cylinder, and is finished with fresh gas. As a rule, it heats only when receiving fresh gas. and is then soon finished (in from 12 to 24 hours). At first the liquid is only tepid; then much froth appears in the man-hole, and the temperature rises a good deal. At last the liquid turns pink; and now the froth mostly (but not always) vanishes again. The operation may be considered finished when a sample taken out of the man-hole settles quickly and completely, leaving comparatively little sediment, and the liquid shows a deep pink colour, smells of chlorine (no longer of hydrochlorous acid), and bleaches litmus-paper. So long as it is not finished (*i. e.* contains hypochlorite) it gives off streams of chlorine when mixed with hydrochloric acid

*cold*; afterwards it does not do this. Batches of 24° Tw. usually settle better and of a darker pink than those of 28°. The pink colour is generally ascribed to the formation of permanganate from manganese mechanically carried over or contained in the lime. Opl (Dingl. Journ. ccxv. p. 237) and Blunt (Chem. News, xxxiv. p. 171) assert the colouring-matter to be calcium ferrate; but Davis (Chem. News, xxxiv. p. 183) distinctly asserts the presence of manganese in all pink-coloured solutions of calcium chlorate and bleach-liquor, as well as the direct spectroscopical proof of the presence of permanganic acid.

When a cylinder cannot be finished all at once, but the work must be interrupted (*e. g.* on account of Sunday), it takes much longer time before the temperature rises and the chlorate is formed. In such cases, heating by steam, which is quite unnecessary otherwise, would be in place. A similar thing happens if instead of water or weak washings a concentrated solution is employed, and of course less lime is added; here also the liquid does not heat and will not turn pink. Hence it is best to divide such concentrated liquors, *e. g.* that of the reserve cylinder C, among several absorbers. Without a certain amount of heat no chlorate is formed, but only bleach-liquor;

$$2CaO + 4Cl = CaCl_2 + Ca(OCl)_2;$$

the calcium hypochlorite, when more chlorine is admitted, decomposes into chlorate and chloride with evolution of heat, but without absorbing any more chlorine;

$$3Ca(ClO)_2 = Ca(ClO_3)_2 + 2CaCl_2;$$

so that, on the whole, 5 molecules of calcium chloride fall to 1 of chlorate. Why this decomposition is complete only when an excess of chlorine is present, and then takes place without much loss of oxygen, is not known; the spontaneous evolution of heat seems to show that a more complicated reaction than is apparent from the formula may take place. It is possible to assume that the excess of chlorine with the hypochlorite first forms hypochlorous acid

$$(CaCl_2O_2 + 4Cl = CaCl_2 + 2Cl_2O),$$

and that the later oxidizes a further quantity of calcium hypochlorite to chlorate, chlorine being liberated again.

$$(CaCl_2O_2 + 4Cl_2O = CaCl_2O_6 + 8Cl);$$

but such an assumption of simultaneous absorption and evolution of chlorine in the liquid, although not impossible, can only be maintained on the strength of distinct data, which as yet are wanting.

The process never goes on without some loss of oxygen. According to the equation there ought to be in the finished liquor exactly 1 mol. chlorate to 5 mol. chloride; but it is very rarely possible to get below 5·3 mol. of the latter; 5·4 or 5·5 are still acceptable, but even 5·6 to 5·8 mols. chloride occur to 1 mol. chlorate. In the French works the absorbers are purposely cooled, to lessen the loss by evolution of oxygen; whether with great success is not proved. Since of the 0·3 to 0·5 mol. of calcium chloride in excess a portion is always to be accounted for by ths hydrochloric acid never absent from chlorine, very little remains for any chloride formed by loss of oxygen from chlorate; but during the hot French summers possibly more than the above loss may occur unless the liquid is cooled. According to experiments made in the author's laboratory, a solution of calcium chlorate and chloride as obtained in this process, showed exactly the same percentage when it was tested fresh, and after many hours' boiling; so that the loss of oxygen, if any such really occur, must take place before the hypochlorite has been converted into chlorate.

As soon as the contents of a cylinder have been completely changed into chlorate, according to the tests mentioned above, the gas is cut off, and the whole, clear liquor and mud together, is run through the large bottom cock into the settlers; the cylinder is at once recharged with water or washings and lime, and is now made the last of the set.

The *settlers*, E E (fig.100), are best built up of cast-iron plates; when made of wood and lined with lead, they are liable to be often needing repair. They are so much lower than the absorbers that they can be filled from any of these by means of a large spout with plug-holes. More settlers are needed if the mud is washed in the settlers themselves than if only the clear liquor is run off and the mud washed in different vessels. The clear liquor is run off by means of a swivel siphon inside the settler, similar to those mentioned in other places. The swivel pipe is kept in its place by a chain or a thin curved iron rod. Fig. 104 shows a double swivel for lowering the pipe parallel with the front of the settler, as seen from above; fig. 105 is a perforated drum surrounding the mouth of the pipe and covered with canvas, by means of which the liquid

can be drawn off lower down without carrying away any mud. An iron spout running along all the settlers takes the clear liquor from all the pipes to a well, I, from which a pump, H, pumps them into

Fig. 104.

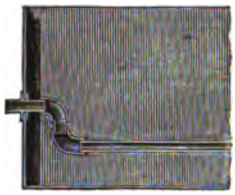
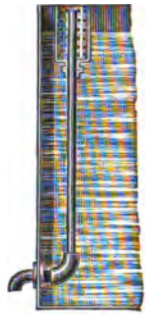


Fig. 105.



the higher tanks K or L. But rarely can the absorbers be placed high enough for giving a fall not only to the settlers, but also from these to the pans, and from these to the crystallizing-coolers; by such an arrangement the pumping of the strong liquors is saved, but not that of the washings, which have to go back into the absorbers. The well I must have two partitions, I′ and I″, so as to keep the strong liquor always separate from the washings: the former only is sent into the pans; and its volume must be accurately known. The height of the strong liquor before and after running it off from E, and thus the bulk of the liquor sent into the tanks, is ascertained—which is absolutely necessary in order to calculate the amount of potassium chloride (muriate) to be added. After running off the strong liquor, the *mud* is either discharged into other vessels for further treatment, or, as we have assumed in the drawing, it is washed with water in E itself so long as the hydrometer shows any salt in the liquor; and the washings, run into I″, are pumped into the reservoir L, from which they are taken as wanted, instead of part of the fresh water, for charging the cylinders A. The washed mud is discharged through a plug-hole in the bottom of the settler, or by shovelling out; it consists of silica, clay, calcium carbonate, and a little calcium hydrate, and is of no further use. The operation of washing it would be very much simplified and improved by employing a filter-press; and the same holds good of the muddy residues obtained afterwards in the boiling-down pans and the dissolver for crude salt.

The clear solution of calcium chlorate and chloride is now to be boiled down. Formerly the *boiling-down pans* were made of lead, and consequently subject to the rapid wear and frequent damage incidental to this material. Here also, as well as in every other portion of the plant for manufacturing crude chlorate, lead has been replaced by cast iron or even wrought iron, without damaging the quality of the chlorate, which must in any case be recrystallized.

The choice can only be between wrought-iron or cast-iron pans. The latter have certain advantages, especially in being less acted upon by the liquor: but the former are cheaper, can be made of all sizes, and are not liable to crack; so that they are decidedly preferable, and the more so if the free chlorine, which alone could damage them, is removed by adding a very small quantity of soda waste to the liquor run out of the pans, as this instantly destroys its smell and colour and prevents any corrosion afterwards of either the pans or the pumps.

The pans have the same shape as the "boat pans" described in Vol. II. p. 506 to 508, and are set exactly in the same manner. They ought to be covered with planks and possess a draught-pipe to carry the chlorine given off at first to the chimney; but this is quite unnecessary if the above-mentioned treatment with tank-waste has been carried out. Two pans 8 ft. × 20 ft. × 3 ft. suffice for the apparatus described; their waste heat passes underneath the small pans Q Q, which are placed at a higher level and serve for dissolving the crusts and mud from the pans P P, the dissolving residue, and the washings from refining, and running the clear liquor into the pans P P; as this liquor already contains *potassium* chlorate, not calcium chlorate, it must be sent directly into the pans. The pans P P are run off by swivel pipes, just like the settlers E E.

We have already seen that the volume of the clear liquor sent from the settlers E into the pan is gauged. At the same time a sample is taken, tested for chlorate in the laboratory, and the addition of potassium chloride calculated from this test. One might think that, if the quantity of lime charged into the absorbers remained the same, or, at least, if the specific gravity of the clear liquor in E were the same, there would be always the same quantity of potassium chloride required for effecting the decomposition. But this is not the case; and as the potassium chloride (or, to call it by its commercial name, the *muriate of potash*) is the dearest of all

the raw materials employed, it is not advisable to add any considerable excess. Still less will it do to add too little; for any calcium chlorate, being very soluble, would remain in the mother liquors. There are many processes for estimating chlorate; but the following is probably the easiest and quickest. A solution of about 100 grams of pure crystallized ferrous sulphate and 100 grams strong vitriol is made up to one litre, and its value ascertained by daily titration with seminormal potassium permanganate (*i. e.* one containing 15·82 grams pure crystallized salt per litre, and indicating 0·004 gram. oxygen per cub. cent.). Suppose that each 25 cubic centims. of iron solution require 20·5 of permanganate, a certain quantity of the chlorate-solution is pipetted into a flask, boiled till all free chlorine is expelled, cooled, and a sufficient quantity of iron-solution added, the flask closed with an india-rubber cork and a Bunsen's valve (Vol. I. p. 55, fig. 3), or with a twice bent tube, the outer limb of which dips into water contained in a beaker; heat is applied, the liquor kept fully boiling for a few minutes and then cooled, during which the closing of the valve or the coming back of the water from the beaker prevents any oxidation by the atmospheric oxygen. All the chlorate is now converted into chloride or sulphate; and a corresponding quantity of ferrous sulphate is converted into ferric sulphate:

$$CaCl_2O_6 + 12FeO = CaCl_2 + 6Fe_2O_3.$$

All the oxygen of the chlorate is spent in peroxidizing the iron salt.

The liquor is now retitrated with permanganate; thus the quantity of ferrous sulphate consumed, and consequently that of the chlorate, is found. It is not necessary to follow up all these processes every time by calculations; the permanganate corresponding to the chlorate (*i. e.* that required for standardizing the iron-solution, less that consumed in retitrating) shows the amount of the chlorate at once by a simple factor, and that of the necessary potassium chloride by another. As seminormal permanganate solution (*i. e.* a solution of 15·82 grams $KMnO_4$ in 1 litre of water) gives off 0·004 oxygen per cub. cent., and since 122·6 parts of $KClO_3$ yield 48 of oxygen, the former must show per cubic centim. $\frac{122 \cdot 6}{12}$ $= 0 \cdot 01021$ $KClO_3$ or 0·00621 KCl. Suppose the commercial muriate employed to contain 95 per cent. KCl, the last factor will

become $\frac{0{\cdot}00621 \times 100}{95} = 0{\cdot}006537$. Hence, if 2 cub. cent. of the chlorate liquor have been employed, if this has taken up iron equivalent to 15·5 cub. cent. permanganate, each litre of the liquor will require an addition of $15{\cdot}5 \times 500 \times 0{\cdot}006537$ grams of 95-per-cent. muriate. If the calculation is to be simplified still more, the factor is made to contain once for all the number of litres per centimetre (or inch) of the height gauged. If the settlers were exactly $3 \times 2$ metres, each centimetre of their height would be $=60$ litres; hence, if for each testing 2 cub. cent. of liquid are taken, the constant factor for 95-per-cent. muriate upon a consumption of $x$ cub. cent. permanganate becomes $x \times 500 \times 60 \times 0{\cdot}006537 = 196{\cdot}11\,x$. That is, for each cub. centim. of permanganate used in testing 2 cub. centims. chlorate liquor, each centimetre of the height of the settlers requires 196·11 grams 95-per-cent. muriate of potash. It will be easy to apply this calculation to any given size of settler, and to English instead of metrical measures.

This calculation shows at the same time in stock-taking how much loss there has been in crystallizing, refining, &c.; it points out, and frequently permits stopping, any sources of loss.

There is always some excess over the theoretical quantity of potassium chloride added, to compensate for any inaccuracy of reading off the height of the acid, &c.; an addition of 3 per cent. above the calculated quantity will suffice in most cases. It is decidedly advisable to employ the purest muriate, nearly free from sodium chloride, in spite of its comparatively higher price; for all this sodium chloride gets mixed with the potassium chlorate, renders it more difficult to be purified from chlorides in refining, and causes loss by increasing the quantity of mother liquors. Upon 10 parts of potassium chlorate actually obtained, $8\frac{1}{2}$ to 9 parts of good muriate of potash are needed.

Sometimes the muriate is added already in the absorbing-cylinders, but mostly only in the boiling-down pans; in the former case, of course, the muriate cannot be calculated exactly. The opinion now and then held, and probably forming the ground of that proceeding, viz. that calcium chlorate inclines more to decomposition than potassium chlorate, is entirely unfounded.

The potassium chloride required for a batch is put into the pans directly after running-in the first portion, or, still better, as soon as this has been brought to ebullition; and the boiling-down is

continued, feeding the pan with fresh liquor either continuously or by instalments, till the proper degree of concentration has been attained. The procedure is not the same in all places. Some evaporate the liquor at once down to 70° Tw. (measured hot) and allow it to crystallize; the mother-liquors then contain so little chlorate that they cannot be worked for it. Others only boil down to 50° or 55° Tw., and after crystallization evaporate the mother liquors once more to 71° Tw. By the latter plan perhaps a little more chlorate is obtained; but it is doubtful whether the increased labour, consumption of fuel, and mechanical losses do not outweigh that advantage. The second portion of salt is very impure, and must be recrystallized twice, while the first plan (which we will describe in detail) requires only one recrystallization of all the salt.

When the pans are run off, the mud is best kept back by means of a filtering-drum (Vol. II. p. 561, fig. 241); it must be taken out after each operation, lest it burn fast to the pan and cause it to wear out prematurely. The mud is washed in the small pans Q, and the liquor boiled down in the pans M along with the other liquors. The discharge-pipes of the pans M join into an open spout, from which, by means of branch spouts, all the *crystallizing-cones* N N can be filled. Of these a sufficient number should be provided to permit the liquor to remain in them 9 or 10 days in winter, and 14 days in summer. Formerly they were made of wood and lined with lead; but cast iron is preferable, as with care it does not contaminate the salt much more; and it is far better than lead vessels, in consequence of its greater conductivity for heat, and its immunity from leaking. The iron vessels are made just like those employed in making soda crystals, viz. large shallow pans, or oblong pans with rounded corners (Vol. II. p. 566, figs. 242 & 243). They ought to be placed at a slight elevation above the floor, and provided with a plug in the bottom for running out the mothers. On the ground between each two rows of them spouts are laid to receive the mother liquors, which they convey through several wells P P, sunk in the ground for the purpose of catching the salt always carried away. The larger these wells are, and the longer the mother liquors remain in them, the more completely can the fine crystals of chlorate settle; and even the continued cooling acts favourably in this respect. A canvas filter in front of the drainage-pipe is also very useful for retaining small crystals. In a factory in the south of France, where the climate calls for it more than in England, all the summer mother

liquors are preserved in large tanks right through the winter; and in this way an extra crop of ¼ lb. of chlorate per cubic foot of liquor is obtained. The salt collecting in the catch-wells is mostly too impure to be refined directly, and is either simply put back into the pans M M, or else it is recrystallized once more.

When the time is up, the plug in the bottom of each crystallizing-cone is lifted, at first gently, so that but little salt gets out along with the mothers; most of this can be retained by a canvas bag suspended below the plug-hole. If no plug-hole is provided, a lead siphon is employed, the outer limb of which does not end in the spout, but in a bucket, where a good deal of salt is caught. When most of the mother liquor is run off, the salt, which is easily detached from the sides, is heaped up round the plug-hole, allowed to drain, and then put into special *drainers* O O, made of wood, lined with lead, with a perforated false bottom. These drainings run away along with the former mother liquors, with which they are identical in composition; but afterwards the adhering mother liquor is washed off by pouring water over the salt from a watering-can, and as some chlorate will be dissolved now, these washings are run into a separate well and pumped back into the pans. This work is much better done by a small (even a hand-worked) centrifugal machine, in which the washing and draining are done much more completely. The washing is greatly facilitated by the stoutly acicular shape of the crude crystals. If among these are large, clear, transparent prisms of hydrated calcium chloride, this proves that the boiling-down has gone too far, which happens most readily in winter time, and must be remedied by concentrating to one degree of the hydrometer less. The washing is not continued very long, in order that there may not be too many diluted liquors; but if it be interrupted too soon, the liquors will have to be changed all the sooner in recrystallizing.

The *mother liquors* ought, before running to waste, to be regularly tested for their percentage of calcium chlorate and of potash. Of the former (calculated as $KClO_3$) the maximum usually present is 25 grams per litre, or 25 ounces per cubic foot; the best result known to the author is 17·5 grams. But with bad work 35 grams per litre and upwards are found, which means a considerable loss, and so much the more as most endeavours to work this liquor, which is also a saturated solution of calcium chloride, for chlorate, or even for chlorine (by boiling with hydrochloric acid) have been

in vain. When too much chlorate is in it, this may be caused by the evaporation not having gone far enough, or by the cooling not having lasted long enough. But it may also be caused by a deficiency of potassium chlorate permitting calcium chlorate to remain undecomposed; this is discovered by an estimation of the potash (with platinum chloride), which should show at least 10 grams KCl per litre in excess of that required by the chloric acid present. But it also happens that on putting the muriate into the pans the men do not stir it up well enough, so that a portion of it may remain at the bottom and afterwards be wanting in the liquor.

In the best case about 10 or 12 per cent. of all the potassium chlorate remain in the mother liquors, which are as yet entirely lost; and it would be a very grateful task to discover a practicable process for obtaining this valuable salt from them.

Weldon proposed employing *magnesia* in the place of lime for manufacturing potassium chlorate. The reaction in either case is the same; but the residue contains, in lieu of calcium chloride, magnesium chloride, from which, by evaporation to dryness in a current of steam and calcining, magnesia and hydrochloric acid are regenerated. This process has succeeded very well in many experiments made by Weldon on a small scale; but on a large scale it has never been tried yet, probably because the incomplete decomposition of magnesium chloride into MgO and HCl has been established otherwise.

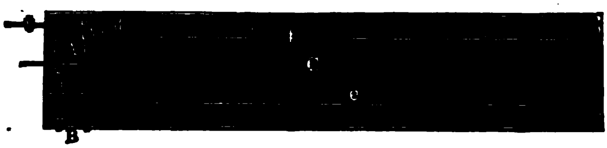
### *Recrystallizing (Refining) the Crude Salt.*

The latter is not a commercial article; its colour, sometimes nearly white, but often brown or reddish, the shape of its crystals, and its chemical impurities, necessitate its purification by dissolving, settling, and recrystallizing, mostly followed by washing the crystals. One of two plans is followed here. In the one the dissolving and crystallizing are one continuous process; in the other they are successive operations.

The first (continuous) method is carried out as follows. A wooden cistern lined with lead (fig. 106) 40 feet long, $7\frac{1}{2}$ feet wide, and $1\frac{1}{2}$ foot deep, is divided into three compartments, A, B, and C. A ($4 \times 5\frac{1}{2}$ feet) serves for dissolving; B ($4 \times 2$ feet) for filtering; the largest compartment C, for crystallizing. In A there is a lead steam-pipe *a*, which is laid in several coils and comes out sideways,

carrying out the condensed water; in this compartment the crude salt is put, either on a sieve or in a bag, and is dissolved by heating

Fig. 106.



with indirect steam in the mother liquor coming over from C through the siphon *d*. Thus at the bottom of A a hot saturated solution collects, which is continuously pumped by the small pump *b*, over the sieve *c* (covered with very densely woven calico) into B. Since pumping cannot be avoided here, and the application of steam-power is not well adapted for such light work, a contrivance driven by water-power is employed (which is shown in fig. 107). To the roof two hangers, *b*, are fixed, with rings in which a flat iron rod, *a*, with pivoted ends, turns. *a* carries on one side the arm *c*, to which the plunger *d* is suspended. This is made of wood, covered with lead, and travels loosely in the small pump-barrel *e*, closed at the bottom, with an outlet-pipe *f* at the top and inlet valve *g* near the bottom. The latter need not close tightly; it is only made of a round piece of india-rubber a little larger than the aperture in *e*, hung from a nail above the latter, and stiffened at the back by a bit of lead. The iron rod *h* is fixed in the same horizontal planc as *c*, and sends out arms on both sides of *a*. On the side opposite to *c* it carries, in a fork curved downwards, the tipping bucket *i*, which is shown separately in fig. 108. Its pivots are below its centre of gravity, so that, when empty, it hangs down straight with the assistance of the small weight *k*. But when *i* is filled with water so far that the centre of gravity is above the pivots, its equilibrium becomes unstable, the bucket tips over, empties itself, and at once rights itself again by means of the weight *k*. The water for filling the bucket runs from the regulating cock *n*, through the pipe *m*, connected by a flexible tube *o* with the stiff tube *p*, which has an outlet into the bucket *i*.

The apparatus works in this way. When the cock *n* is opened, the bucket *i* is gradually filled with water and becomes heavier. As the rod *a* turns in the rings *b*, the bucket *i* will go down and

turn the rod partly round its axis; the flexible connexion at *o* permits the water-pipe *p* to follow. At the same time the arm *c*

Fig. 107.

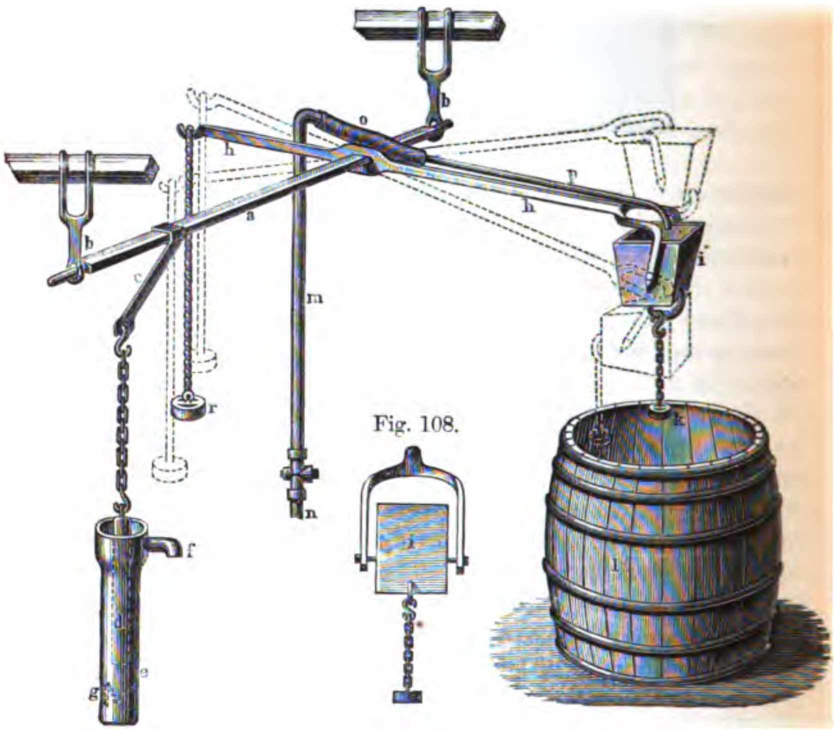


Fig. 108.

rises, and along with it the plunger *d*. Consequently liquor will run into *e* by the valve *g*. As soon as *i* has arrived at the lowest point, it tips and then rights itself again; and this side is now so much lighter than the other, that the rod *a* suddenly turns back. In order to assist this a weight *r* is suspended by a cord from that arm of *h* which is on the same side as *c*. This, together with the weight of *d* itself, causes *a* to turn suddenly, and at the same time *c* to go down, and *d* to enter the barrel *e*. By this a certain quantity of liquid is forced out of *f* into its place of destination.

The length of rope is so regulated that the weight *r* strikes upon the floor or upon a bracket, &c., before *d* has descended quite to the bottom of *e*; this prevents damage to the latter by the sudden

shock. Immediately afterwards the bucket *i* begins to fill again and the play begins anew. The water running out of *i* and that running out of *p*, during the tipping, run into the tub *l*, and may be used for any purpose.

A special advantage of this kind of pump is, that travelling ever so slowly it can never "lose its charge." By regulating the cock *n* the filling of *i* can be hastened at will; and this regulates the number of strokes. The quantity of the liquid running out is regulated by the plunger *d*, which can be made to dip more or less by means of its chain. This apparatus works very well, and gives no trouble.

The hot chlorate liquor, pumped in this way into B (fig. 106), and filtered through *c*, can enter from B into C by a 1-inch aperture at about $\frac{1}{3}$ of the height of the latter. In C it is forced by the board *e* to travel to its other end and forward again before it can get to the siphon *d*, also kept apart by a board *f*. Since only about half a gallon of liquid is sent every two or three minutes into B, this small quantity does not cause any sensible disturbance or current in the large space of C; on the contrary, the liquid is quickly cooled there, and gradually deposits crystals, which constantly grow, and become largest in the part furthest from the compartments A and B. When the liquor has arrived at the siphon *d*, it is quite cooled down and is drawn off by the latter (which is constantly filled, and the orifice of which in A is narrowed down to $\frac{3}{8}$ inch) into A at the same rate as the pump sends hot liquor over into B.

Thus the work is perfectly continuous; the mother liquor, saturated in A with crude salt, is pumped into B, filtered, run through C, cools there, deposits its excess of salt in a pure form, and returns through the siphon *d* just in proportion as it is wanted. Once a week the salt accumulated in C is fished out (with a shovel of hard wood or copper); it is best to cease dissolving a day before. From time to time, when the mother liquor has become too impure, it must be pumped back to the boiling-down pans for crude salt, and fresh water must be put into the dissolver. This ought to stand on a water-tight floor, and be a little raised, so that, in case of leakage, the liquor running out may be saved.

This plan of crystallization is best adapted for crude salt deprived almost entirely of mother liquor, and also for salt obtained by evaporating to only 50° or 55° Tw.; it takes but little labour and

supervision. But it is not so well adapted for suddenly increased or decreased demands upon the production; hence it is not so much to be recommended as the second plan (*dissolving in special vessels* and slowly crystallizing), in which the concentration can be regulated at will and larger crystals can be made.

In this case the crude salt, already deprived of mother liquor, is dissolved by water and steam in iron or wooden cylinders lined with lead, about 6 feet wide and high. Iron vessels it is best to surround with a non-conducting jacket. The steam is not employed directly, but in a coil of lead pipe, passing outwards again; its waste portion may be used for heating the drying-plates (see below).

The liquor is run off best by a swivel pipe, the top of which carries a perforated drum (Vol. II. p. 561) with a double canvas cover, as here every impurity must be kept out. Each such tank can dissolve 6 or 7 cwt. of crude salt. The liquor is made up to 25° Tw.; at 26° it is already too concentrated, crystallizes too quickly, and yields too small crystals.

For dissolving, half mother liquor from refining and half condensed steam-water from the drying-plates are taken; the rest of the mother liquor is pumped back into the crude-salt pans; and thus an accumulation of impurities in these liquors is prevented. The dissolving takes place at a full boiling-heat. When the solution has got up to strength, it is allowed to settle for two hours, and, by gradually turning down the swivel pipe, is then run into one of the coolers. Having been already filtered by the canvas-covered drum, it is filtered a second time by a canvas bag suspended at the end of the leaded-out spout which conveys the hot liquor into the crystallizing-cones. The residue from dissolving is put back into the pans Q Q (fig. 101), and thus again enters into the crude salt.

*The crystallizing-cones for the finished salt* must be placed in a very clean special shed; its bottom, made of asphalt, stone flags, or some other tight material, should incline towards a catch-well, to save any thing spilt. The cones themselves are usually made of wood and lined with lead, with their bottoms boat-shaped or oval, or inclined to one side—all for facilitating the running-off of the mother liquors. The cones are made of pretty strong planks, in order to cool slowly and furnish large crystals. For the same purpose planed laths are put into the cones, upon which the finest

crystals are found. The crystallization takes eight or nine days in winter, or fourteen days in summer. In the deepest part of each cone there is a plug-valve for running-off the mother liquor into a well, from which it is pumped, in part to the dissolver, in part back to the crude-liquor pans. The crystals are drained in the cones themselves, and again in canvas bags suspended in wooden frames. They are washed with steam-water (from the drying-plate) till the chlorides are almost entirely removed. The most tenacious is the lead chloride; but this can always be kept out by adding in the dissolving a little (say ½ lb.) pure soda ash, by which the lead and some lime are precipitated as carbonates, and also mechanically carry down any suspended flakes of ferric hydroxide. The removal of the lead can be effected even more completely by adding a small quantity of sodium sulphide. With proper treatment the chlorides in the potassium chlorate can be got down to 0·05 per cent. When the evaporation and crystallization of the crude salt has been carried on in iron vessels, very little lead is contained in the chlorate; but the presence of some has been distinctly shown, *e. g.* by Hilger (Wagner's Jahresb. 1871, p. 446).

The washed salt is dried on a hollow iron plate, like those used in calico-printing works, but placed horizontally and covered with lead. It is possible to dry upwards of 1 cwt. per square yard of surface in 12 hours. The drying-plates can be heated by the waste steam from dissolving, pumping, and grinding, direct steam from the boiler making up the deficiency. At the other end there is an automatic apparatus for discharging the condensed water without allowing any steam to escape. This water is collected in a well, which is lined with lead, and employed for washing the finished and dissolving the crude salt.

The crystals are now sifted through a sieve with 8 holes to the linear inch, or less, as required; the powder falling through is ground while still warm (when quite cold it is apt to cake together), in a small horizontal mill like a flour-mill, between granite stones, or "French burrs," to an impalpable powder, which it is best to drive, in a cylinder sieve with rotating brushes, through miller's gauze. There is no danger in grinding if the admixture of organic substances (wood, straw, &c.) or iron (nails, &c.) is avoided, and if care is taken that the bearings do not get heated, especially the "eye" of the bottom stone (through which the spindle passes). If the latter precaution be neglected, an explosion may take place.

Chlorate is usually packed in hundredweight casks laid out with blue paper. Powder and crystals fetch the same price. In regular work about 2 or 3 parts of crystals are obtained to 1 part of powder. The latter ought to be of a snow-white colour and as fine as flour. without any grittiness. The crystals ought to be pretty large plates, but thin, brilliant and transparent, not porcelain-like; the latter may easily occur from excessive drying.

The *examination* of chlorate of potash is usually done by dissolving a large quantity (by which a perfectly clear solution must be produced, as any impurities, especially of an organic nature, may cause very unpleasant consequences in using the chlorate) and testing for chlorides and sulphates by silver nitrate and barium chloride. The latter should not be present at all, the former only in faint traces (see above). Iron or lead would be detected by ammonium sulphide.

The *cost* of chlorate of potash will, of course, differ very much, according to whether the chlorine is made from native manganese or by the Weldon process. By Deacon's process also chlorate has been made; and this seems to be very appropriate, since the drying of the gas by sulphuric acid is unnecessary, and any contamination by carbonic acid would do no harm. But, on the other hand, the dilution with indifferent gases must make a *complete* conversion into chlorate difficult, although Weldon found that a partial conversion into chlorate is unavoidable when dilute chlorine gas is passed into milk of lime. In any case Deacon's process is used only in one or, at most, in two places for this product.

It is generally assumed that 1 part of potassium chlorate requires 6⅔ times as much chlorine as 1 part of bleaching-powder; hence, with native manganese containing 70 per cent. $MnO_2$, about 6 tons will be required for 1 ton of chlorate. The latter moreover requires 17 to 18 cwt. of good (90–95-per-cent.) muriate of potash. Theoretically, only 12¼ cwt. of pure KCl or 13¼ cwt. of 90-per-cent. muriate are required; the remainder is lost, principally in the mother liquor—partly as such, partly as chlorate. Besides, about 2½ to 3 tons of lime, and about 4 or 5 tons of coals are needed for evaporating, dissolving, and steam for the engines, apart from the fuel required for manufacturing the chlorine. The amount of labour in proportion to the scale of the manufacture differs so much that no general statements can be made about it; it is pretty much the same whether 2 or 8 cwt. are turned out per diem. One man attends to the absorbers, another to the pans and

the crystallization of the crude salt, a third and a boy to the refining and grinding; when more is made, one or two men are wanted for getting the lime &c.

According to experiments by F. Hobrecker (cited by Mylius in Hofmann's Bericht, 1875, i. p. 127, but without stating whether they were made on the large or the small scale), 100 parts of potassium chloride require

| | | |
|---|---|---|
| 4431·0 | parts | hydrochloric acid of 32° Tw., |
| 772·0 | „ | 65-per-cent. manganese, |
| 418·0 | „ | lime, |
| 72·7 | „ | 92-per-cent. potassium chloride, |
| 2262·0 | „ | brown coal. |

[Acid, manganese, coals, and lime are set down much too high, potassium chloride too low.]

Roscoe and Schorlemmer (Lehrbuch, ii. 58) state the quantities required for manufacturing 1 ton of chlorate of potash as follows—about 37 to 40 tons hydrochloric acid of sp. grav. 1·15, 16 to 20 cwt. of potassium chloride, 3 tons lime, 5½ tons 70-per-cent. manganese, and 10 to 12 tons coal.

Chlorate of potash is *employed* for manufacturing lucifer matches (especially the so-called Swedish kind), for pyrotechnical purposes, for fuses, &c., also for dyeing and calico-printing (as an oxidizing agent, *e. g.* for aniline black), in the fusion of alizarine, and for oxidations in some other industrial branches; but mostly it is too expensive. It is used in laboratories for preparing oxygen—and in medicine, especially for gargling in cases of inflammation of the throat, &c.; but large quantities act poisonously, like those of other potassium salts.

The *extent of production* can only be stated with approximate accuracy for England, where the royalty paid to the Weldon Company gives an idea of it; it may be assumed to be 1300 tons per annum in that country. A considerable quantity is also made in the south of France (at Salindres alone 22 cwt. per day); smaller quantities in Germany and Austria.

### *Chlorate of Soda* ($NaClO_3$).

Since this salt, owing to its solubility far exceeding that of the potassium salt, has largely come into use, especially for aniline black in calico-printing, we shall briefly treat of its properties and

preparation. It forms colourless crystals of the regular system, frequently plate-shaped. They present peculiar hemihedral faces and corresponding phenomena of circular polarization, pointed out by Marbach (Poggend. Annal. xci. 482, xciv. 412, xcix. 451). The salt is stable in the air; when heated it fuses and yields perchlorate, without evolving much oxygen. According to Kremers (ib. xcvii. p. 4) 100 parts of water dissolve

| at 0° | 20° | 40° | 60° | 80° | 100° | 120° C. |
|---|---|---|---|---|---|---|
| 81·9 | 99 | 123·5 | 147·1 | 175·6 | 232.6 | 333·3 parts $NaClO_3$. |

The boiling-point of the saturated solution is at 132°.

The specific gravities of solutions at 19°·5 C. are,

| for 10 | 15 | 20 | 25 | 30 | 35 per cent. $NaClO_3$. |
|---|---|---|---|---|---|
| 1·070 | 1·108 | 1·147 | 1·190 | 1·235 | 1·282 |

It dissolves at 16° in 34 times its volume of alcohol of 83 per cent., and less amounts of alcohol at higher temperatures.

According to Schloesing (Compt. Rend. lxxiii. p. 1272) sodium chloride influences the solubility of sodium chlorate thus: 100 parts of water at 12° dissolve 89·3 $NaClO_3$ or 35·77 NaCl; but when both salts are present in excess, 50·75 $NaClO_3$ and 24·4 NaCl are dissolved. At 122° C. 100 parts of water dissolve 249·6 $NaClO_3$ and 11·5 NaCl; and on cooling down to 12° C. they retain 68·6 $NaClO_3$ and all the NaCl (11·5). This behaviour is noticeable with regard to the preparation of the salt.

Chlorate of soda is usually made from chlorate of potash by means of hydrofluosilicic acid. One way of doing this is, decomposing chlorate of potash by hydrofluosilicic acid, separating the solution of chloric acid formed from the precipitated potassium fluosilicate, and saturating the chloric acid by soda; the solution of sodium chlorate is evaporated and cooled down for crystallization.

Or else the hydrofluosilicic acid is saturated with soda and the solution of sodium fluosilicate boiled with potassium chlorate, whereby a solution of sodium chlorate is formed directly. The hydrofluosilicic acid might be regenerated from the potassium fluosilicate by heating it with sulphuric acid and passing the evolved mixture of silicon tetrafluoride and hydrofluoric acid into water.

Hydrofluosilicic acid has been made on a very large scale in apparatus similar to blast-furnaces, as described in Vol. II. p. 317.

For the present purpose it must be made on a smaller scale, which can be easily done by heating a mixture of fluorspar, sand, and concentrated sulphuric acid in a cast-iron retort, and passing the silicon tetrafluoride into water, where it decomposes into hydrofluosilicic acid and silica:

$$3SiFl_4 + 2H_2O = 2H_2SiFl_6 + SiO_2.$$

The gelatinous silica might give some trouble by stopping up the gas-pipe, &c.; but this can be prevented in various ways—for instance by passing the silicon tetrafluoride gas, not through a column of water, but through a channel in which it will come into contact with constantly moistened surfaces, such as a tower loosely packed with bricks. In a German patent (No. 9072, May 30, 1879) Zenisek and Schmidt describe an apparatus for this purpose. The silicon tetrafluoride, given off in a long cast-iron retort, is absorbed by water contained in a vessel provided with an agitator, which constantly breaks up the silica separating on the top of the water, and thus offers always a fresh surface of water to the action of the gas.

Sodium chlorate can also be made, exactly like the potash salt, by first preparing calcium chlorate precisely as described above, and decomposing this by sodium chloride. In this case, however, there is very much sodium chlorate lost in the mother liquors, in which it cannot very well be separated from calcium chloride.

# APPENDIX I.

## COST OF ERECTING AN ALKALI-WORKS.

The following hints on the cost of plant of an alkali-works must necessarily be taken with all possible reserve. Great divergences will occur in this respect between different countries, between different parts of the same country, and even in the same neighbourhood at different periods. Nay, it may even happen that, of two factories erected at the same time and not far from each other, one costs much more than the other, either on account of a much higher sum to be paid for the land, or for levelling the ground, or securing the foundations. Special plant is necessary for connecting the factory with a railway-line, a canal, or a navigable river; the railway-embankments, quays, wharves, elevators, &c. frequently require a large outlay of capital. Some factories, again, require long sewers for getting rid of their waste liquids; some must have a good deal of land for depositing their rubbish and waste; or, if situated near the sea-coast, they must have hopper-barges to take the waste out to sea. Of course the following statements cannot include these things.

Apart from all these considerations, and from the differences of prices in various localities, the cost of plant, properly speaking, is decisively influenced, first, by the *scale of working*, and, secondly, by the more or less substantial *style of erection*. Every body knows that generally a large works costs comparatively less to build than a small one; but to this there are many exceptions. As a rule large works are built more substantially and with more regard to appearance than small ones; they also require certain machinery and appliances which would be quite out of place in

small factories—such as railways, locomotive engines, lifting-gear, cranes, packing-machines, pumps, agitators, &c. This should lessen the cost of *manufacturing*; but it raises the cost of *plant*.

In order to start from a secure basis, the following statements will refer to a medium-sized works, producing 120 tons of 52-per-cent. alkali per week, principally as estimated by the author in 1874 to 1875 for the north of England upon actual data. Even the prices then prevailing have mostly been assumed here. It appeared useless to substitute other prices, which would be wrong again in a few years' time, and, in any case, for other parts. Still it seemed advisable to put in the prices such as they were, so as to convey some idea of the cost to those who refer to this chapter for information.

For a few of the apparatus, for which the author did not himself possess the data, these have been supplied to him by Mr. Schaffner, of Aussig. They refer to the Aussig works in 1879, and comprise the shelf burner for pyrites smalls, the muffle furnace (blind roaster) for salt-cake, the condensation of hydrochloric acid by the Aussig system, and the recovery of sulphur from the tank-waste.

The number and size of the various portions of plant will be understood from the following considerations. In order to manufacture 120 tons of soda ash per week, or 20 tons per day, 28½ tons of sulphate must be made. This corresponds to 23¾ tons of pure NaCl, or, say, 25½ tons of common salt. Such a quantity can be made in two open roasters, if the work is pushed very hard; but at most factories only from 9 to 10 tons of salt are decomposed per furnace; and even in those first mentioned a third furnace will be desirable as a reserve in case repairs are needed. We shall assume three open roasters, which should suffice under all circumstances. As an alternative we must assume *four* blind roasters; for although the above quantity of salt might possibly be turned out of three blind furnaces, this would mean pushing them very hard, and a fourth furnace ought to be provided to supply the deficiency during repairs. On the Continent six blind roasters would be employed.

The condensation of the *hydrochloric acid* requires at least four stone condensers, $6 \times 6 \times 50$ feet; but by providing each with three stone cisterns for preliminary condensation, they will be amply sufficient. It is assumed that each condenser supplies two pans or two roasters. As an alternative, the cost of the same condensers

if built of bricks in tar and sand is subjoined. Lastly, the cost of the Aussig system of condensation is given; this, however, applies only to blind furnaces, decomposing about 4 tons of salt per day.

28½ tons of sulphate require about 22 tons of the strongest *vitriol,* which can be made from 15½ tons of 48-per-cent. pyrites, in lead chambers of a capacity of at least 266,000 cubic feet, or, say, 7 chambers $20 \times 19 \times 100$ feet. We shall assume 8 chambers, so as to leave one over for repairs or rebuilding, which will sometimes leaves a little acid for sale. 40 ordinary pyrites-burners and 5 dust-burners will do the work.

In order to work up the sulphate, we should have at least 8 *black-ash* furnaces, making 24 batches of 3 cwt. each, with another furnace for repairs, or two *revolvers* of the size described in Vol. II. p. 406.

We assume that a portion of the soda ash is made into *crystals;* but in this case the *calcining* (*carbonating*) *furnaces* can be reduced in number.

As far as *bleaching-powder* is concerned, the quantity of salt decomposed will, with proper work, yield 10 tons of 35-per-cent. bleach per day, and, with blind roasters, perfect condensation, and proper management, leave some hydrochloric acid to spare for *sulphur-recovery.* The latter, by Schaffner's or Mond's process, should yield 2 tons 8 cwt. of sulphur per day, and will require 6 tons of hydrochloric acid of 33° Tw.

## I. *General.*

*Land.*—There will be at least 5 acres required; but, if possible, there should more. The site should be adjacent to a navigable river or a canal, or so near a railway line that it can be connected with it by a branch line. An *indispensable* condition is the possibility of running away weak acid or alkaline liquids. Equally indispensable is a large supply of water, whether pumped from a river or a well, or brought in pipes from a distance. The following important items must be provided; but it is impossible in this place to state even any approximate figures for the same.

| | £ | £ | £ |
|---|---|---|---|
| Land | | | |
| Paving and fencing in | | | |
| Well and pump, or aqueduct | | | |
| Levelling and excavations in general | | | |
| Drains and sewers | | | |

| | | | | £ | £ | £ |
|---|---|---|---|---|---|---|
| Railways to and within the works, railway-carriages, engines, &c. | | | | | | |
| Wharf, crane, lighters, canal barges | | | | | | |
| Office and draughtsman's room, with furniture | ...... | ...... | ...... | 300 | | |
| Laboratory and implements | ...... | ...... | ...... | 250 | | |
| Blacksmith's, fitter's, carpenter's, plumber's shops | ...... | ...... | ...... | 250 | | |
| Machinery and tools therein | ...... | ...... | ...... | 200 | | |
| Cooperage and implements thereof | ...... | ...... | ...... | 250 | | |
| Gas-works, gas-pipes, and fittings | ...... | ...... | ...... | 750 | | |

## II. *Sulphuric-acid Works.*

| | | At £ s. | £ s. | £ |
|---|---|---|---|---|
| Chamber-house (all wood) in the usual style | ...... | ...... | ...... | 250 |
| N.B. On the Continent, where the chambers are roofed in in a substantial building, this item amounts to about £2130. | | | | |
| 40 pyrites-burners, back to back; each:— | | | | |
| Brickwork | ...... | ...... | 9 10 | |
| Cast-iron front plates with planed doors cwt. | 25 | ...... | 15 0 | |
| Grate-bars, bearers, and other iron-work cwt. | 12 | ...... | 6 0 | |
| Excavations, foundation. sundries | ...... | ...... | 3 10 | |
| | | | 34 0 | 1360 |
| 5 dust-burners, Schaffner's system (Vol. I. p. 219), 5 feet 4 inches × 11 feet × 13 feet high, each:— | | | | |
| Common brickwork | ...... | ...... | 8 10 | |
| Fire-brickwork | ...... | ...... | 40 0 | |
| Ironwork tons | 3 | ...... | 30 0 | |
| | | | 78 10 | 392 |
| 4 nitre-ovens (semicylindrical troughs), each | ...... | 13 10 | 54 0 | |
| Carriage, erection, brickwork | | ...... | 21 0 | |
| | | | | 75 |
| Pipes for burner-gas, 2½ feet wide, 40-feet. tons | 9½ | ...... | 120 0 | |
| Pillars, and erection | ...... | ...... | 20 0 | |
| | | | | 140 |
| 8 vitriol-chambers 100×20×19, 6-lb. lead. | | | | |
| Lead for chambers, straps, pipes, mountings, tons | 224 | ...... | 4928 0 | |
| Zinc, nails, small stores | ...... | ...... | 80 0 | |
| Timber for floors, ceilings, side frames, &c. | ...... | ...... | 1100 0 | |
| Plumber's work (contract) | ...... | ...... | 200 0 | |
| Carpenter's work (contract) | ...... | ...... | 225 0 | |
| 192 cast-iron H-shaped pillars 20 feet high, at 12½ cwt., together tons | 120 | 9 0 | 1080 0 | |
| Foundations and erection | | | 200 0 | |
| Levelling ground and sundries | | | 387 0 | |
| | | | | 8200 |
| 2 Glover towers and 2 Gay-Lussac towers; the former 9 feet square × 30 feet high, made of 14-lb. lead, the bottom of 35-lb. | | | | |
| Carried forward | ...... | ...... | ...... | 10417 |

| | | At £ s. | £ s. | £ |
|---|---|---|---|---|
| Brought forward ................. | ...... | ...... | ...... | 10417 |
| lead; the latter 6 feet in diameter, 50 feet high, 6-lb. lead. Weight of lead, exclusive of cisterns, &c. ..................... tons | 34 | ...... | 748 0 | |
| Zinc, nails, small stores.......................... | ...... | ...... | 20 0 | |
| Timber for frames, roofs, cisterns ........... | ...... | ...... | 170 0 | |
| Firebricks and flints for lining and packing the Glover towers ............................ | ...... | ...... | 60 0 | |
| Coke for packing the Gay-Lussac towers ... | ...... | ...... | 50 0 | |
| Foundations ...................................... | ...... | ...... | 150 0 | |
| Plumber's contract ............................ | ...... | ...... | 150 0 | |
| Carpenter's contract ............................ | ...... | ...... | 140 0 | |
| Air-pumping engine, erected ................. | ...... | ...... | 150 0 | |
| 2 acid-eggs, pipes and connexions ........... | ...... | ...... | 150 0 | |
| Excavations and sundries.......................... | ...... | ...... | 212 0 | |
| | | | | 2000 |
| 3 steam-boilers 6 feet 6 inches diameter, 26 feet long, with setting and mountings (comp. *Alkali-Works*) .......... .................... | ...... | ...... | 800 0 | |
| Steam- and water-pipes and erection ......... | ...... | ...... | 200 0 | |
| | | | | 1000 |
| Chimney ........................................... | ...... | ...... | ...... | 300 |
| Total ................................ | ...... | ...... | ...... | 13717 |

## III. *Decomposing.*

| | | | | |
|---|---|---|---|---|
| Buildings for decomposing-house, sulphate- and salt-shed ................................... | ...... | ...... | ...... | 800 |
| Decomposing-furnaces:— | | | | |
| Either 3 *open furnaces*, each 7 feet × 26 feet. | | | | |
| Brickwork ...................................... | ...... | ...... | 75 0 | |
| Ironwork (front plates, binders, dampers, pipes, tools, barrows, &c.).................. | ...... | ...... | 90 0 | |
| Pan ........................................... tons | 6 | 11 0 | 66 0 | |
| Excavations, sundries ........................ | ...... | ...... | 39 0 | |
| | | | 270 0 | 810 |
| Or 4 *blind roasters* (muffles) each 12 × 42 feet. | | | | |
| Common brickwork .......................... | ...... | ...... | 60 0 | |
| Fire-brickwork ................................ | ...... | ...... | 224 0 | |
| Ironwork ...................................... | ...... | ...... | 100 0 | |
| Pan .............................................. | ...... | ...... | 66 0 | |
| | | | 450 0 | [1800] |
| Gas-pipes: 1st, fireclay pipes for pan-gas, inclusive of tarring, erecting, and carrying-frames ................................ feet | 300 | ...... | 110 0 | |
| 2nd, metal pipes, 2-feet, for open-roaster gas, 300 feet .................................. tons | 33 | 12 0 | 396 0 | |
| Erecting, supporting-columns, &c. ............ | ...... | ...... | 104 0 | |
| | | | | 610 |
| N.B. For blind roasters only fireclay pipes are required, so that the total cost is only £220, or £390 less than the above. | | | | |
| Chimney............................................. | ...... | ...... | ...... | 300 |
| Total .................. ............. | ...... | ...... | ...... | 2520 |

## IV. *Condensation of Hydrochloric Acid.*

| | | At £ s. | £ | s. | £ |
|---|---|---|---|---|---|
| *Either* four *stone condensers*, 6×6×50 feet inside, each :— | | | | | |
| Flags for condenser itself, superficial feet ... | 1600 | ...... | 210 | 0 | |
| Freestone for foundations (20 feet deep) cubic feet | 1000 | ...... | 50 | 0 | |
| Packing of coke or fire-bricks .................. | ...... | ...... | 27 | 0 | |
| Timber for uprights, stays, cisterns, &c. cubic feet | 550 | ...... | 40 | 0 | |
| Labour, foundation (contract) .................. | ...... | ...... | 50 | 0 | |
| Labour, stone-mason.............................. | ...... | ...... | 75 | 0 | |
| Labour, blacksmith, fitter, carpenter ......... | ...... | ...... | 40 | 0 | |
| Labour, excavating, yard-labour, &c. ......... | ...... | ...... | 30 | 0 | |
| Pump for water, pipes, cocks, connexions ... | ...... | ...... | 50 | 0 | |
| Ironwork, pitch, tar, fireclay, sundries ...... | ...... | ...... | 100 | 0 | |
| *Three stone cisterns*, 7×5×5 feet inside: together, flags.............. superficial feet | 730 | ...... | 90 | 0 | |
| Foundations ........................................ | ...... | ...... | 30 | 0 | |
| Labour, stone-mason (contract) ............... | ...... | ...... | 30 | 0 | |
| Iron, pitch, tar, fireclay, pipes, sundries...... | ...... | ...... | 20 | 0 | |
| | | | 842 | 0 | 3368 |
| *Or* four *brick condensers*, 18 inches thick. | | | | | |
| Foundation as above............................. | ...... | ...... | 100 | 0 | |
| Flags for bottom, top, and shelves ............ | ...... | ...... | 38 | 0 | |
| Brickwork and packing, with labour ......... | ...... | ...... | 125 | 0 | |
| Timber as above ................................ | ...... | ...... | 40 | 0 | |
| Labour of carpenter, blacksmith, fitter ...... | ...... | ...... | 40 | 0 | |
| Labour for excavating .......................... | ...... | ...... | 20 | 0 | |
| Iron, pitch, tar, fireclay, sundries ........... | ...... | ...... | 92 | 0 | |
| Pump and pipes as above ....................... | ...... | ...... | 50 | 0 | |
| Three stone cisterns as above .................. | ...... | ...... | 170 | 0 | |
| | | | 675 | 0 | 2700 |
| *Or* 6 sets of *Aussig condensers*, as described Vol. II. p. 242, each of which supplies a blind roaster decomposing 4 tons of salt per day. (Probably, as English blind roasters have a larger output, only four furnaces and four sets of condensers would be required, augmenting the number of Woulfe's bottles; but we shall give the estimate as received from the Aussig Chemical Works, which supplies this condensing-plant all complete from its own pottery.) Each set comprises :— | | | | | |
| 2 stoneware towers (one for pan-gas, the other for roaster gas), of 11 pipes each, packing of stoneware dishes, radiated cover for distributing the water, "sight" for observing the gas, &c. .......... | | | 90 | 0 | |
| 110 Woulfe's bottles with connecting (cooling-) pipes, and all other pipe connexions.......... | | | 240 | 0 | |
| Foundations .......... | | | 50 | 0 | |
| Wood frame for the towers .......... | | | 70 | 0 | |
| Two stone cisterns for cooling the gas and condensing the impure hydrochloric acid (containing $SO_4H_2$) .......... | | | 50 | 0 | |
| Sundry small plant, cocks, glass tubes, &c. .......... | | | 25 | 0 | |
| | | | 525 | 0 | 3150 |
| N.B. This does not comprise the pipes conveying the gas from the furnace to the stone cisterns; but as the cooling is done subsequently, these pipes need be only short, and would be much cheaper than estimated above for the usual condensing-towers. | | | | | |

## V. *Alkali-Works.*

| | | At £ s. | £ s. | £ |
|---|---|---|---|---|
| *Buildings* for furnaces and lixiviating-tanks... | ...... | ...... | 2000 0 | |
| Warehouses of all kinds ........................ | ...... | ...... | 800 0 | |
| Engine and mill-house ........................ | ...... | ...... | 150 0 | |
| Large chimney (or several smaller ones)...... | ...... | ...... | 750 0 | |
| Underground main flues and channels ...... | ...... | ...... | 400 0 | |
| | | | | 4100 |
| *Black-ash furnaces.* | | | | |
| Either 8 *hand-furnaces*, each :— | | | | |
| Brickwork .................................. | ...... | ...... | 70 0 | |
| Ironwork (front plates, binders, grates, dampers, tools, bogies, &c.) .............. | ...... | ...... | 73 0 | |
| Boiling-down pan, 18×9×2 feet...... tons | 4½ | 10 0 | 45 0 | |
| Black-salt drainer, 15×4×3½ feet ... ton | 1½ | ...... | 27 0 | |
| Red-liquor pump ........................ | ...... | ...... | 6 0 | |
| Foundation and sundries .................. | ...... | ...... | 29 0 | |
| | | | 250 0 | [2000] |
| Or 2 *revolvers*, each :— | | | | |
| Revolver with engine, erected (tender of 1875) | ...... | ...... | 1120 0 | |
| 2 boiling-down pans, 28×8 feet ......... tons | 7 | 18 0 | 126 0 | |
| 2 drainers, 25×4 feet ........................ | 5 | ...... | 90 0 | |
| Red-liquor pump, engine, pipes ............ | ...... | ...... | 50 0 | |
| Ironwork for binding, grates, &c. ............ | ... .. | ...... | 100 0 | |
| Brickwork, concrete foundations, &c. ......... | ...... | ...... | 300 0 | |
| Railway above the furnace, and pillars for it | ...... | ...... | 150 0 | |
| Hoist for the charging-materials (half-cost) . | ...... | ...... | 75 0 | |
| 12 waggons for black ash (tender) ........... | ...... | ...... | 54 0 | |
| 2 large waggons for charging (tender) ...... | ...... | ...... | 43 0 | |
| Sundries .......................................... | ...... | ...... | 42 0 | |
| | | | 2150 0 | 4300 |
| *Lixiviating-tanks*, 2 sets of 5 each. 10×10×6 feet ...................................... tons | 36 | 15 0 | 540 0 | |
| Overflow and connecting pipes, spouts, cocks, &c. ............................................ | ...... | ...... | 150 0 | |
| Labour of blacksmith and fitter ............... | ...... | ...... | 75 0 | |
| Foundations ...................................... | ...... | ...... | 75 0 | |
| Liquor-wells and settlers .................. tons | 13 | ...... | 195 0 | |
| 2 pumps and engines ........................ | ...... | ...... | 80 0 | |
| Sundries .......................................... | ...... | ...... | 85 0 | |
| | | | | 1200 |
| 8 *Calcining-* (carbonating- or finishing-) *furnaces*, each :— | | | | |
| Brickwork ........................................ | ...... | ...... | 42 0 | |
| Iron fronts, binders, grate-bars, tools, barrows.. ............................................ | ...... | ...... | 60 0 | |
| Foundations, &c. ................................ | ...... | ...... | 11 0 | |
| N.B. This work would be done by one Mactear carbonator and two hand-wrought furnaces. The cost of a Mactear carbonator, including a pan for boiling liquor by the waste heat, is about £1470, that of the brickwork &c. belonging to it about £300. | | | 113 0 | 904 |
| Carried forward.................... | ...... | ... | ...... | 10504 |

| | | At £ s. | £ s. | £ |
|---|---|---|---|---|
| Brought forward | ...... | ...... | ...... | 10504 |
| *Machinery* &c | | | | |
| 4 steam-boilers, 6 feet 6 inches diam., 30 feet long, fired inside ...................... tons | 50 | ...... | 1000 0 | |
| Setting, mountings, and erecting .............. | ...... | ...... | 500 0 | |
| Boiler-shed ......................................... | ...... | ...... | 100 0 | |
| 30 H.P. steam-engine for mills &c............ | ...... | ...... | 300 0 | |
| Mills for alkali and chalk........................ | ...... | ...... | 300 0 | |
| Smaller engines for sundries ................. | ...... | ...... | 150 0 | |
| Elevators or cranes ............................. | ...... | ...... | 150 0 | |
| Weigh-bridges (one for railway trucks, one for carts)........................................... | ...... | ...... | 300 0 | |
| Steam-pipes and cocks .......................... | ...... | ...... | 200 0 | |
| Shafting ............................................. | ...... | ...... | 200 0 | |
| Auxiliary machinery .............................. | ...... | ...... | 300 0 | |
| | | | | 3500 |
| *Crystallizing-plant* for 90 tons crystals per week (saves half of the carbonating-furnaces). | | | | |
| Buildings ........................................... | ...... | ...... | 1000 0 | |
| Dissolver, with machinery ..................... | ...... | ...... | 250 0 | |
| Hoist for ash ...................................... | ...... | ...... | 50 0 | |
| Settlers ...................................... tons | 10 | 15 0 | 150 0 | |
| Staging, pipes, &c. ............................... | ...... | ...... | 60 0 | |
| 120 crystallizing-cones, cast iron, 8×9×1¼ feet...................................... tons | 255 | 8 10 | 2167 0 | |
| Spouts, drying-benches, &c. ................... | ...... | ...... | 80 0 | |
| Pump, well, and settler for mother liquors... | ...... | ...... | 100 0 | |
| Boiling-down pan, drainer, and furnace for same ................................................. | ...... | ...... | 200 0 | |
| Weigh-bridge and sundries ..................... | ...... | ...... | 113 0 | |
| | | | | 4170 |
| *Sulphur-Recovery* (Schaffner's process) for 37 tons wet waste per diem, yielding 1 ton 8 cwt. sulphur. | | | | |
| 20 wrought-iron cisterns, 17×8½×4 ft. tons | 50 | 15 0 | 750 0 | |
| Pipes and cocks for liquors, steam, and air... | ...... | ...... | 200 0 | |
| Liquor-tanks (made of wood) ................. | ...... | ...... | 60 0 | |
| Shed for precipitating, melting, and packing sulphur ............................................ | ...... | ...... | 300 0 | |
| 2 precipitating-tubs (wood), 10 feet diam., 6 feet high, with agitating-gear and mounting ........................................... | ...... | ...... | 57 0 | |
| 6 H.P. steam-engine for agitating and pumping, with shafting and pulleys.............. | ...... | ...... | 105 0 | |
| Fan-blast with 5 H.P. engine ................. | ...... | ...... | 75 0 | |
| 1 melting-boiler for sulphur, 4 feet outside, 10 feet long, 3 feet inside ............... tons | 3⅛ | ...... | 75 0 | |
| Smaller boilers, moulds for sulphur, sundries | ...... | ...... | 100 0 | |
| | | | | 1722 |
| N.B. Unless steam can be obtained from the main boilers, a 15 H.P. steam-boiler is required for this part of the process. | | | | |
| Total .................................. | ...... | ...... | ...... | 19896 |

## VI. *Bleaching-Powder* (60 tons per week).

(Comp. p. 212 for detailed tenders for machinery.)

| | | At £ s. | £ s. | £ |
|---|---|---|---|---|
| 4 large chlorine-stills, 7×7×10 feet inside, each:— | | | | |
| Flags | ...... | ...... | 75 0 | |
| Stone-mason's work (contract) | ...... | ...... | 25 0 | |
| Blacksmith and plumber | ...... | ...... | 7 0 | |
| Iron work and lead | ...... | ...... | 9 0 | |
| Stoneware cocks, pipes, india-rubber, &c. | ...... | ...... | 10 0 | |
| Foundations and sundries | ...... | ...... | 29 0 | |
| | | | 155 0 | 620 |
| 4 small stills for native manganese, 7×5×4 feet inside, each:— | | | | |
| Flags | ...... | ...... | 33 0 | |
| Iron, lead, stoneware | ...... | ...... | 8 0 | |
| Mason's contract | ...... | ...... | 10 0 | |
| Sundry labour | ...... | ...... | 5 0 | |
| Foundation and sundries | ...... | ...... | 14 0 | |
| | | | 70 0 | 280 |
| 2 neutralizing-wells, 14 feet wide, 7 feet deep, 15 inches thick, stonework, together:— | | | | |
| Stones ... cub. feet | 1750 | ...... | 88 0 | |
| Mason's labour | ...... | ...... | 38 0 | |
| Excavating, tar and sand, puddling, sundries | ...... | ...... | 74 0 | |
| Steam-engine and agitators | ...... | ...... | 150 0 | |
| Pumping-engine, with 6-inch ram | ...... | ...... | 88 0 | |
| Pipes and connexions | ...... | ...... | 50 0 | |
| Foundations for machinery &c. | ...... | ...... | 12 0 | |
| | | | | 500 |
| 3 still-liquor settlers, wrought iron, 16×12 ×6 feet, together ... tons | 13 | 15 0 | 195 0 | |
| Foundations and woodwork of the large stagings | ...... | ...... | 300 0 | |
| | | | | 495 |
| 6 mud-settlers, as above ... tons | 26 | 15 0 | 390 0 | |
| Valves, swivel pipes, pipes, spouts, &c. | ...... | ...... | 75 0 | |
| | | | | 465 |
| Apparatus for washing the neutralizing-mud | ...... | ...... | ...... | 300 |
| 3 oxidizers, 10 feet wide, 30 feet high...... tons | $22\frac{1}{2}$ | 15 0 | 337 0 | |
| Valves at top and bottom | ...... | ...... | 27 0 | |
| Steam- and air-pipes | ...... | ...... | 105 0 | |
| Blowing-engine, erected | ...... | ...... | 550 0 | |
| Air-vessel | ...... | ...... | 20 0 | |
| Staging and testing-cabin | ...... | ...... | 120 0 | |
| Sundry pipes, &c. | ...... | ...... | 41 0 | |
| | | | | 1200 |
| 3 milk-of-lime vessels, with machinery for stirring | ...... | ...... | 260 0 | |
| Lime-pump, pipes, foundations | ...... | ...... | 120 0 | |
| | | | | 380 |
| Carried forward | ...... | ...... | ...... | 4240 |

| | | At £ s. | £ s. | £ |
|---|---|---|---|---|
| Brought forward ................. | ...... | ...... | ...... | 4240 |
| 2 steam-boilers, with setting, mountings, and shed (comp. alkali) ......................... | ...... | ...... | ...... | 800 |
| 6 bleaching-powder chambers, 80×24×6 feet, of 5-lb. lead ............................. tons | 48 | 22 0 | 1056 0 | |
| Timber for frames ................................ | ...... | ...... | 270 0 | |
| Asphalt floor, laid down ......... superf. feet | 11,500 | ...... | 215 0 | |
| Plumber's contract................................ | ...... | ...... | 72 0 | |
| Carpenter's contract .............................. | ...... | ...... | 90 0 | |
| Excavating and sundries ......................... | ...... | ...... | 147 0 | |
| | | | | 1850 |
| 6 lime-kilns, 14×11½×6¼ feet, with wood bracing .......................................... | ...... | ...... | ...... | 360 |
| Buildings .......................................... | ...... | ...... | ...... | 500 |
| Total ................................. | ...... | ...... | ...... | 7750 |

*Ground-plan of an Alkali-works.*

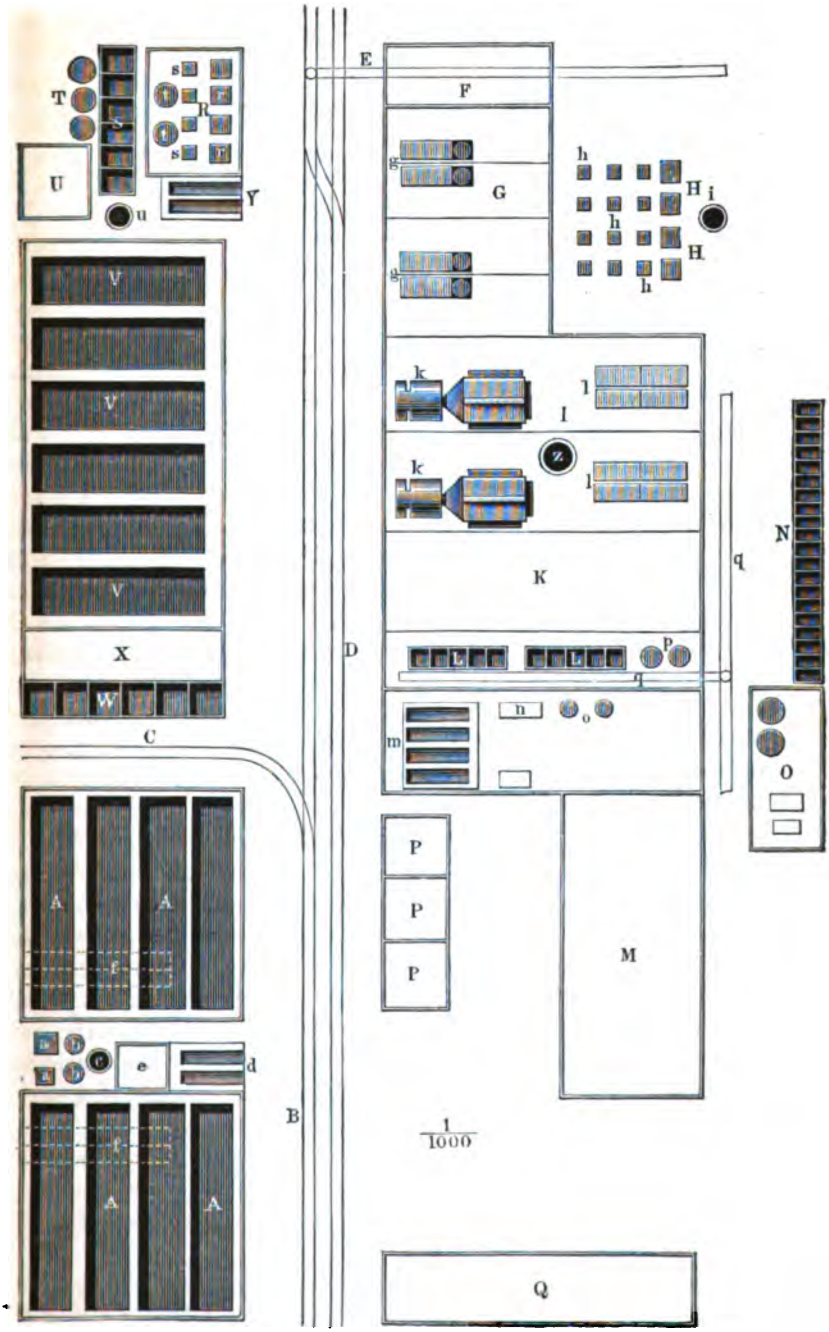
The estimate just given will be better understood from the ground plan (fig. 109), which shows a works of the size spoken of on a scale of $\frac{1}{1000}$. The buildings are all as large as required; and sufficient space is allowed within for all operations round the furnaces and machinery; but the free yard-space is here contracted to a minimum, and should, if at all possible, be several times as much, in order to admit of materials being deposited and enlargements made. Still the plan as it is shows a suitable disposition of the several portions of the factory; so that one department works into the hands of that next following with as little shifting of solid material as possible, whilst the liquid acids are allowed to run greater distances, as this entails no expense.

Soda crystals and caustic are not provided for; there would not be room for them on the ground as laid out here.

A A are the vitriol-chambers; *a a*, the Glover towers; *b b*, the Gay-Lussac towers; *c*, the chimney; *d*, the chamber boilers; *e*, the engine-house for the air-pump and acid-eggs. The pyrites-kilns, *f f*, are underneath the chambers, as well as the store of nitre, of acid, carboys, and pyrites, so far as the latter does not lie alongside the railway B, where it arrives. This line, B, also serves for taking away the burnt ore.

The branch C may also serve for conveying pyrites, but principally for chalk or limestone, to supply the black-ash furnaces and lime-kilns. Consequently the yard-space round it ought to be, if

Fig. 109.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at all possible, much larger than in the plan. The line D conveys principally coals, which, as is apparent, can be laid down in front of most of the furnaces. The branch line E passes straight through the salt-warehouse F. This adjoins the decomposing-house G, one side of which serves as a warehouse for sulphate, whilst the other is taken up by the decomposing-furnaces and pans *g g*. *h h* are the cisterns belonging to the hydrochloric-acid condensers H H; *i* is the chimney belonging to this department. The condensers might be placed on the other side, so as to be nearer the chlorine-stills; but then the decomposing-furnaces would be more distant from the railway.

Immediately adjoining the decomposing-house is the black-ash house I, containing the two revolvers *k k* and the eight carbonating furnaces *l l*. Eight hand-worked black-ash furnaces would occupy about as much space as the revolvers, if placed back to back similarly to the carbonating-furnaces. *z* is the principal chimney. K serves as a ball-flat, adjoining the lixiviating tanks L L. *m* is the range of boilers belonging to this department; *n*, the engine; *o*, mills; *p*, carbonating-cylinders. The calcined ash from the furnace is stored near the mills, the ground and packed ash in the warehouse M.

The tank-waste is conveyed outside on the line *q*, and is tipped out for oxidation; it is lixiviated and again oxidized in the tanks. N O is the house for precipitating and melting the sulphur. P P, workshops for blacksmiths, fitters, carpenters, coopers, &c. Q, offices, laboratory, and warehouse for small stores. There is also a little yard-space left here.

The hydrochloric acid runs direct from the condensers H H, which are placed at a sufficient height, to the still-house R, containing the mud-stills *r r*, the native-manganese stills *s s*, and the neutralizing-wells *t t*. S are the manganese mud-settlers, above them the still-liquor settlers; T, the oxidizers; U, the engine-house for the blowing-engine; Y, the steam-boilers; *u*, the chimney; V V, the bleaching-powder chambers, placed on pillars so that the room underneath can serve for packing and warehousing the bleaching-powder. W, the lime-kilns; X, the space for slaking and sifting the lime.

# APPENDIX II.

## ADDENDA TO VOL. I.

To p. 42. *Action of sulphuric acid upon lead.*—A paper by Mactear (Chem. News, xli. 236) on this subject chiefly cites the information contained in the text, and adds a few experiments confirming the same.

To p. 44. *Analysis of sulphuric acid and pyrosulphuric acid.*—Since fuming oil of vitriol or solid pyrosulphuric acid cannot be mixed with water without some danger, their dilution, for the purpose of titrating them, is usually effected as follows. A certain quantity is quickly weighed off in a small beaker, which is placed at the bottom of a large beaker; the latter is covered by a large dished glass, and a little water sprinkled against the joint, where it is retained by capillarity. Thus a moist atmosphere is produced within the beaker; and after 24 hours the acid is found to have attracted enough water to be diluted without any danger of spurting. The process can be very much hastened by covering the bottom of the large beaker with about an inch of water, and heating the whole gently in the water bath, so that the drops, slowly condensing from the steam, fall one by one into the small beaker.

Cl. Winkler prepares both the solid pyrosulphuric acid and the sulphuric anhydride for analysis by gently warming the vessels on a sand bath, till the acids have been liquefied. The sulphuric anhydride does not liquefy completely; but the composition of the liquid and the gelatinous portion are practically identical. He now takes up a certain quantity (say 5 or 10 cubic centims.) by means of a pipette, weighs it off in a small stoppered bottle of thin glass, after having put about 10 or 15 cub. centims. of ordinary strong sulphuric acid into it, and ascertained its weight (the strength of that acid being known once for all). The two acids are mixed, in which process a great deal of heat is given off; the cooled mixture can be poured into water without any danger; the bottle is rinsed out, and the whole liquid reduced to a certain volume, of which a

portion is titrated by standard potash solution in the ordinary manner.

It is even more convenient to ascertain the strength of the acid by means of the hydrometer; and this can be done not merely with such acids as are liquid at the ordinary temperature, but also with pyrosulphuric acid, which, after being liquefied, can be cooled down to 20° C. without crystallizing at once; so that time remains for reading-off the hydrometer. From his experiments Winkler has calculated the following table, in which column *a* gives the specific gravity at 20° C., *b* the percentages of $SO_3$ and $H_2O$, *c* that of $SO_3$ present along with ordinary strong oil of vitriol (testing 66° with Baumé's, or 170° with the ordinary Twaddle's hydrometer), *d* free $SO_3$, real monohydrate ($SO_4H_2$), and water.

*Percentage of Fuming Oil of Vitriol at different Specific Gravities.*

| *a.* Spec. grav. at 20° C. | *b.* Percentage of | | *c.* Percentage of | | *d.* Percentage of | | |
|---|---|---|---|---|---|---|---|
| | $SO_3$. | $H_2O$. | $SO_3$. | Ordinary strong vitriol. | free $SO_3$. | real $SO_4H_2$. | $H_2O$. |
| 1·835 | 75·31 | 24·69 | .... | 100·00 | .... | 92·25 | 7·75 |
| 1·840 | 77·38 | 22·62 | 8·39 | 91·61 | .... | 94·79 | 5·21 |
| 1·845 | 79·28 | 20·72 | 16·08 | 83·92 | .... | 97·11 | 2·89 |
| 1·850 | 80·01 | 19·99 | 19·04 | 80·96 | .... | 98·01 | 1·99 |
| 1·855 | 80·95 | 19·05 | 22·85 | 77·15 | .... | 99·16 | 0·84 |
| 1·860 | 81·84 | 18·16 | 26·45 | 73·55 | 1·54 | 98·46 | |
| 1·865 | 82·12 | 17·88 | 27·57 | 72·43 | 2·66 | 97·34 | |
| 1·870 | 82·41 | 17·59 | 28·76 | 71·24 | 4·28 | 95·76 | |
| 1·875 | 82·63 | 17·37 | 29·95 | 70·05 | 5·44 | 94·56 | |
| 1·880 | 82·81 | 17·19 | 30·38 | 69·62 | 6·42 | 93·58 | |
| 1·885 | 82·97 | 17·03 | 31·03 | 68·97 | 7·29 | 92·71 | |
| 1·890 | 83·13 | 16·87 | 31·67 | 68·23 | 8·16 | 91·84 | |
| 1·895 | 83·43 | 16·66 | 32·52 | 67·48 | 9·34 | 90·66 | |
| 1·900 | 83·48 | 16·52 | 33·09 | 66·91 | 10·07 | 89·93 | |
| 1·905 | 83·57 | 16·43 | 33·46 | 66·54 | 10·56 | 89·44 | |
| 1·910 | 83·73 | 16·27 | 34·10 | 65·91 | 11·43 | 88·57 | |
| 1·915 | 84·08 | 15·92 | 35·52 | 64·48 | 13·33 | 86·67 | |
| 1·920 | 84·56 | 15·44 | 37·27 | 62·73 | 15·95 | 84·05 | |
| 1·925 | 85·06 | 14·94 | 39·49 | 60·51 | 18·67 | 81·33 | |
| 1·930 | 85·57 | 14·43 | 41·56 | 58·44 | 21·34 | 78·66 | |
| 1·935 | 86·23 | 13·77 | 44·23 | 55·77 | 25·65 | 74·35 | |
| 1·940 | 86·78 | 13·22 | 46·56 | 53·54 | 28·03 | 71·97 | |
| 1·945 | 87·13 | 12·87 | 47·88 | 52·12 | 29·94 | 70·06 | |
| 1·950 | 87·41 | 12·59 | 49·01 | 50·99 | 31·46 | 68·54 | |
| 1·955 | 87·65 | 12·35 | 49·98 | 50·02 | 32·77 | 67·23 | |
| 1·960 | 88·22 | 11·78 | 52·29 | 47·71 | 35·87 | 64·13 | |
| 1·965 | 88·92 | 11·08 | 55·13 | 44·87 | 39·68 | 60·32 | |
| 1·970 | 89·83 | 10·17 | 58·81 | 41·19 | 44·64 | 55·36 | |

To p. 50. *Impurities of commercial sulphuric acid.*—Gintl (Chemiker-Zeitung, 1879, p. 653) has found in such acid as much as 5 per cent. ammonium sulphate, which impurity would be very easily overlooked in the usual processes for testing sulphuric acid.

To p. 51. *Detection of arsenic in sulphuric acid.*—According to Filhol it is best to generate hydrogen for Marsh's test not by means of sulphuric acid, but by means of zinc or aluminium and caustic potash, because in this case no antimony is volatilized as antimoniuretted hydrogen. In the presence of phosphorus the flame becomes of a fine green colour.

To p. 52. *Detection of nitrous acid.*—Griess (Berliner Berichte, xi. 624) has found extremely sensitive reagents for $N_2O_3$ in *diamidobenzoic acid* (1 : 3 : 5), which gives a distinct yellow colour with one five-millionth part of $N_2O_3$,—and in *metaphenylendiamine*, which shows the same even for 0·1 mg. in a litre, passing over into triamidobenzene. Even a colorimetric estimation of nitrous acid can be founded upon this behaviour.

To p. 69. *Tables for facilitating the use of the Nitrometer.*—The first two of these may be employed for reducing the volume of any gas to 0° C. and a pressure of 760 millims.; the third table facilitates the calculation of the reduced volume of gas into definite nitrogen compounds. The tables are used as follows.

I. *Reduction of the volume found to a temperature of 0° C.* The volume of gas read off on the nitrometer is looked for in the first column, and the figure is noted which is found in the same horizontal line and in the vertical column corresponding to the observed temperature; the latter is the reduced volume. *E. g.* 20 c. c. at 14°=19·03 c. c. at 0° C. As the given readings of the nitrometer extend down to 0·1 c. c., the table permits the reduction even of the fractions up to 10 c. c., by simply shifting the decimal point; beyond this two figures must be looked for and added up. *E. g.* 9·7 c. c. at 17°=9·13 c. c. at 0°; 25·3 c. c. at 12°=23·95+0·29 =24·24 c. c. at 0°.

II. *Reduction to a mercurial pressure of 760 mm.* The readings are reduced precisely as in the former case; but first the expansion of the mercury in the barometer itself must be allowed for, and its position reduced to 0° C., by deducting for temperatures of 0° to 12° 1 mm., for 13° to 19° 2 mm., for 20° to 25° 3 mm. from the pressure read off. The table, not to make it too bulky, is only calculated for intervals of 2 millims., between which, if necessary,

an interpolation can be easily made mentally. *E. g.* 7·8 c. c. at 736 mm. pressure and 18° C. are to be reduced to 760 mm. We look for the figure in column 734 and obtain 7·53 c. c. In order to reduce this to 0° C., we look for the latter figure in Table I., and arrive at 7·04+0·03=7·07 c. c. Of course it is equally right to employ first Table I. and then Table II. It is quite unnecessary to extend the readings to fractions of degrees of temperature, or of millimetres of pressure, as the accuracy of the nitrometer-readings does not go beyond 0·1 c. c.

The use of Table III. is self-evident.

III. *Table for reducing the volume of nitric oxide,* NO, *reduced to* 0° *and* 760 *mm., to other compounds of nitrogen.*

| NO at 0° 760mm. | N. | NO. | $N_2O_3$. | $N_2O_5$. | $NO_3H$. | $NO_3K$. | $NO_3Na$. |
|---|---|---|---|---|---|---|---|
| c. c. | mg. | mg. | mg. | mg. | mg. | mg. | mg. |
| 1 | 0·627 | 1·343 | 1·701 | 2·417 | 2·820 | 4·521 | 3·805 |
| 2 | 1·254 | 2·686 | 3·402 | 4·834 | 5·640 | 9·042 | 7·610 |
| 3 | 1·881 | 4·029 | 5·103 | 7·251 | 8·460 | 13·563 | 11·415 |
| 4 | 2·508 | 5·372 | 6·804 | 9·668 | 11·280 | 18·084 | 15·220 |
| 5 | 3·135 | 6·715 | 8·505 | 12·085 | 14·100 | 22·605 | 19·025 |
| 6 | 3·762 | 8·058 | 10·206 | 14·502 | 16·920 | 27·126 | 22·830 |
| 7 | 4·389 | 9·401 | 11·907 | 16·919 | 19·740 | 31·647 | 26·635 |
| 8 | 5·016 | 10·744 | 13·608 | 19·336 | 22·560 | 36·168 | 30·440 |
| 9 | 5·643 | 12·087 | 15·309 | 21·753 | 25·380 | 40·689 | 34·245 |

The nitrometer is now made of a slightly different shape from that shown, Vol. I. p. 67. The measuring-tube is made cylindrical throughout, and divided into tenths of a cubic centim.; below 50 cub. cent. a certain space is left to allow for the acid which, in shaking-up the tube, might otherwise get into the india-rubber tube. The pinchcock on the plug of the glass cock is replaced by a bit of glass rod put into a short piece of elastic tubing, which equally prevents the acid remaining in the plug from squirting, and is less in the way during the shaking. The plug is tied to the cock by fine copper wire, to prevent its being jerked out in shaking.

Before the operation the plug is turned so that the funnel does not communicate either with the measuring-tube or with the central bore of the cock. This is easily done, and prevents the acid from getting into that bore.

If the acid contains very much nitre, the tube may be soiled by mercuric sulphate. This is prevented by employing a good deal

*as read off to a Tempe*

[*To face page* 338 (vol. iii.).

| 15° | 16° | 17° | [illegible] | 26° | 27° | 28° | 29° | |
|---|---|---|---|---|---|---|---|---|
| 0·948 | 0·945 | 0·941 | 916 | 0·913 | 0·910 | 0·907 | 0·904 | 1 |
| 1·896 | 1·889 | 1·883 | 132 | 1·826 | 1·820 | 1·814 | 1·808 | 2 |
| 2·844 | 2·834 | 2·824 | 249 | 2·739 | 2·730 | 2·721 | 2·712 | 3 |
| 3·792 | 3·779 | 3·766 | 365 | 3·652 | 3·640 | 3·628 | 3·616 | 4 |
| 4·740 | 4·724 | 4·707 | 481 | 4·566 | 4·551 | 4·535 | 4·520 | 5 |
| 5·688 | 5·668 | 5·648 | 597 | 5·479 | 5·461 | 5·442 | 5·424 | 6 |
| 6·636 | 6·613 | 6·590 | 613 | 6·392 | 6·371 | 6·349 | 6·328 | 7 |
| 7·584 | 7·558 | 7·531 | 730 | 7·305 | 7·281 | 7·256 | 7·232 | 8 |
| 8·532 | 8·502 | 8·472 | 846 | 8·218 | 8·191 | 8·163 | 8·136 | 9 |
| 9·480 | 9·447 | 9·414 | 962 | 9·131 | 9·101 | 9·070 | 9·040 | 10 |
| 10·43 | 10·39 | 10·35 | 107 | 10·04 | 10·01 | 9·98 | 9·94 | 11 |
| 11·38 | 11·33 | 11·30 | 119 | 10·96 | 10·92 | 10·88 | 10·85 | 12 |
| 12·32 | 12·28 | 12·24 | 121 | 11·87 | 11·83 | 11·79 | 11·75 | 13 |
| 13·27 | 13·22 | 13·17 | 133 | 12·78 | 12·74 | 12·70 | 12·66 | 14 |
| 14·22 | 14·17 | 14·12 | 144 | 13·70 | 13·65 | 13·61 | 13·56 | 15 |
| 15·17 | 15·11 | 15·06 | 156 | 14·61 | 14·56 | 14·51 | 14·46 | 16 |
| 16·12 | 16·06 | 16·00 | 158 | 15·52 | 15·47 | 15·42 | 15·37 | 17 |
| 17·06 | 17·00 | 16·94 | 169 | 16·44 | 16·38 | 16·33 | 16·27 | 18 |
| 18·01 | 17·95 | 17·89 | 171 | 17·35 | 17·29 | 17·23 | 17·18 | 19 |
| 18·96 | 18·89 | 18·83 | 18[illegible] | 18·26 | 18·20 | 18·14 | 18·08 | 20 |
| 19·91 | 19·84 | 19·77 | 194 | 19·17 | 19·11 | 19·05 | 18·98 | 21 |
| 20·86 | 20·78 | 20·71 | 20[illegible] | 20·09 | 20·02 | 19·95 | 19·89 | 22 |
| 21·80 | 21·73 | 21·65 | 21[illegible] | 21·00 | 20·93 | 20·86 | 20·79 | 23 |
| 22·75 | 22·67 | 22·59 | 22[illegible] | 21·91 | 21·84 | 21·77 | 21·70 | 24 |
| 23·70 | 23·61 | 23·54 | 23[illegible] | 22·83 | 22·75 | 22·68 | 22·60 | 25 |
| 24·65 | 24·56 | 24·48 | 24[illegible] | 23·74 | 23·66 | 23·58 | 23·50 | 26 |
| 25·60 | 25·50 | 25·42 | 25[illegible] | 24·65 | 24·57 | 24·49 | 24·41 | 27 |
| 26·54 | 26·45 | 26·36 | 26[illegible] | 25·57 | 25·48 | 25·40 | 25·31 | 28 |
| 27·49 | 27·39 | 27·30 | 27[illegible] | 26·48 | 26·39 | 26·30 | 26·22 | 29 |
| 28·44 | 28·34 | 28·24 | 28[illegible] | 27·39 | 27·30 | 27·21 | 27·12 | 30 |
| 29·39 | 29·28 | 29·18 | 29[illegible] | 28·30 | 28·21 | 28·12 | 28·02 | 31 |
| 30·34 | 30·23 | 30·12 | 30[illegible] | 29·22 | 29·12 | 29·02 | 28·93 | 32 |
| 31·28 | 31·17 | 31·06 | 30[illegible] | 30·13 | 30·03 | 29·93 | 29·83 | 33 |
| 32·23 | 32·12 | 32·01 | 31[illegible] | 31·04 | 30·94 | 30·84 | 30·74 | 34 |
| 33·18 | 33·06 | 32·95 | 32[illegible] | 31·96 | 31·85 | 31·75 | 31·64 | 35 |
| 34·13 | 34·01 | 33·89 | 33[illegible] | 32·87 | 32·76 | 32·65 | 32·54 | 36 |
| 35·08 | 34·95 | 34·83 | 34[illegible] | 33·78 | 33·67 | 33·56 | 33·45 | 37 |
| [illegible]6·02 | 35·90 | 35·77 | 35[illegible] | 34·70 | 34·58 | 34·47 | 34·35 | 38 |
| [illegible]6·97 | 36·84 | 36·71 | 36[illegible] | 35·61 | 35·49 | 35·37 | 35·26 | 39 |
| [illegible]7·92 | 37·79 | 37·66 | 37[illegible] | 36·52 | 36·40 | 36·28 | 36·16 | 40 |
| [illegible]8·87 | 38·73 | 38·60 | 38[illegible] | 37·43 | 37·31 | 37·19 | 37·06 | 41 |
| [illegible]9·82 | 39·68 | 39·54 | 39[illegible] | 38·35 | 38·22 | 38·09 | 37·97 | 42 |
| [illegible]0·76 | 40·62 | 40·48 | 40[illegible] | 39·26 | 39·13 | 39·00 | 38·87 | 43 |
| [illegible]1·71 | 41·57 | 41·43 | 41[illegible] | 40·17 | 40·04 | 39·91 | 39·78 | 44 |
| [illegible]2·66 | 42·51 | 42·37 | 42[illegible] | 41·09 | 40·95 | 40·82 | 40·68 | 45 |
| [illegible]3·61 | 43·46 | 43·31 | 43[illegible] | 42·00 | 41·86 | 41·72 | 41·58 | 46 |
| [illegible]4·56 | 44·40 | 44·25 | 44[illegible] | 42·91 | 42·77 | 42·63 | 42·49 | 47 |
| [illegible]5·50 | 45·35 | 45·19 | 45[illegible] | 43·83 | 43·68 | 43·54 | 43·39 | 48 |
| [illegible]6·45 | 46·29 | 46·13 | 46[illegible] | 44·74 | 44·59 | 44·44 | 44·30 | 49 |
| [illegible]7·40 | 47·24 | 47·07 | 47[illegible] | 45·66 | 45·51 | 45·35 | 45·20 | 50 |

| 24° | 25° | 26° | 27° | 28° | 29° | |
|---|---|---|---|---|---|---|
| 46·89 | 46·73 | 46·57 | 46·42 | 46·26 | 46·10 | 51 |
| 47·81 | 47·64 | 47·49 | 47·33 | 47·16 | 47·01 | 52 |
| 48·73 | 48·56 | 48·40 | 48·24 | 48·07 | 47·91 | 53 |
| 49·65 | 49·48 | 49·31 | 49·15 | 48·98 | 48·82 | 54 |
| 50·57 | 50·39 | 50·23 | 50·06 | 49·89 | 49·72 | 55 |
| 51·49 | 51·31 | 51·14 | 50·97 | 50·79 | 50·62 | 56 |
| 52·41 | 52·22 | 52·05 | 51·88 | 51·70 | 51·53 | 57 |
| 53·32 | 53·14 | 52·97 | 52·79 | 52·61 | 52·43 | 58 |
| 54·24 | 54·06 | 53·88 | 53·70 | 53·51 | 53·34 | 59 |
| 55·16 | 54·97 | 54·79 | 54·61 | 54·42 | 54·24 | 60 |
| 56·08 | 55·89 | 55·70 | 55·52 | 55·33 | 55·14 | 61 |
| 57·00 | 56·80 | 56·62 | 56·43 | 56·23 | 56·05 | 62 |
| 57·92 | 57·72 | 57·53 | 57·34 | 57·14 | 56·95 | 63 |
| 58·84 | 58·64 | 58·44 | 58·25 | 58·05 | 57·86 | 64 |
| 59·76 | 59·55 | 59·36 | 59·16 | 58·96 | 58·76 | 65 |
| 60·68 | 60·47 | 60·27 | 60·07 | 59·86 | 59·66 | 66 |
| 61·60 | 61·38 | 61·18 | 60·98 | 60·77 | 60·57 | 67 |
| 62·51 | 62·30 | 62·10 | 61·89 | 61·68 | 61·47 | 68 |
| 63·43 | 63·22 | 63·01 | 62·80 | 62·58 | 62·38 | 69 |
| 64·35 | 64·13 | 63·92 | 63·71 | 63·49 | 63·28 | 70 |
| 65·27 | 65·05 | 64·83 | 64·62 | 64·40 | 64·18 | 71 |
| 66·19 | 65·96 | 65·75 | 65·53 | 65·30 | 65·09 | 72 |
| 67·11 | 66·88 | 66·66 | 66·44 | 66·21 | 65·99 | 73 |
| 68·03 | 67·80 | 67·57 | 67·35 | 67·12 | 66·90 | 74 |
| 68·95 | 68·61 | 68·49 | 68·26 | 68·03 | 67·80 | 75 |
| 69·87 | 69·63 | 69·40 | 69·17 | 68·93 | 68·70 | 76 |
| 70·79 | 70·54 | 70·31 | 70·08 | 69·84 | 69·61 | 77 |
| 71·70 | 71·46 | 71·22 | 70·99 | 70·75 | 70·51 | 78 |
| 72·62 | 72·38 | 72·14 | 71·90 | 71·65 | 71·42 | 79 |
| 73·54 | 73·30 | 73·05 | 72·81 | 72·56 | 72·32 | 80 |
| 74·46 | 74·22 | 73·96 | 73·72 | 73·47 | 73·22 | 81 |
| 75·38 | 75·13 | 74·88 | 74·63 | 74·37 | 74·13 | 82 |
| 76·30 | 76·05 | 75·79 | 75·54 | 75·28 | 75·03 | 83 |
| 77·22 | 76·96 | 76·70 | 76·45 | 76·19 | 75·94 | 84 |
| 78·14 | 77·88 | 77·62 | 77·36 | 77·10 | 76·84 | 85 |
| 79·06 | 78·80 | 78·53 | 78·27 | 78·00 | 77·74 | 86 |
| 79·98 | 79·71 | 79·44 | 79·18 | 78·91 | 78·65 | 87 |
| 80·90 | 80·63 | 80·36 | 80·09 | 79·82 | 79·55 | 88 |
| 81·82 | 81·55 | 81·27 | 81·00 | 80·72 | 80·46 | 89 |
| 82·74 | 82·46 | 82·18 | 81·91 | 81·63 | 81·36 | 90 |
| 83·66 | 83·38 | 83·09 | 82·82 | 82·54 | 82·26 | 91 |
| 84·58 | 84·29 | 84·01 | 83·73 | 83·44 | 83·17 | 92 |
| 85·50 | 85·21 | 84·92 | 84·64 | 84·35 | 84·07 | 93 |
| 86·42 | 86·13 | 85·83 | 85·55 | 85·26 | 84·98 | 94 |
| 87·34 | 87·04 | 86·75 | 86·46 | 86·17 | 85·88 | 95 |
| 88·26 | 87·96 | 87·66 | 87·37 | 87·07 | 86·78 | 96 |
| 89·18 | 88·87 | 88·57 | 88·28 | 87·98 | 87·69 | 97 |
| 90·09 | 89·79 | 89·48 | 89·19 | 88·89 | 88·59 | 98 |
| 91·01 | 90·71 | 90·40 | 90·10 | 89·79 | 89·50 | 99 |
| 91·93 | 91·62 | 91·31 | 91·01 | 90·70 | 90·40 | 100 |

| | 710 | 712 | 714 | 716 | 718 | 720 | 722 |
|---|---|---|---|---|---|---|---|
| 1 | 0·934 | 0·937 | 0·940 | 0·942 | 0·945 | 0·947 | 0·95 |
| 2 | 1·868 | 1·874 | 1·879 | 1·884 | 1·890 | 1·895 | 1·90 |
| 3 | 2·803 | 2·810 | 2·818 | 2·826 | 2·834 | 2·842 | 2·85 |
| 4 | 3·738 | 3·747 | 3·758 | 3·768 | 3·779 | 3·789 | 3·80 |
| 5 | 4·672 | 4·685 | 4·697 | 4·711 | 4·724 | 4·736 | 4·75 |
| 6 | 5·607 | 5·621 | 5·637 | 5·653 | 5·669 | 5·684 | 5·70 |
| 7 | 6·540 | 6·558 | 6·577 | 6·595 | 6·614 | 6·631 | 6·65 |
| 8 | 7·474 | 7·494 | 7·516 | 7·537 | 7·558 | 7·578 | 7·60 |
| 9 | 8·409 | 8·431 | 8·456 | 8·479 | 8·503 | 8·526 | 8·55 |
| 10 | 9·34 | 9·37 | 9·40 | 9·42 | 9·45 | 9·47 | 9·50 |
| 11 | 10·28 | 10·31 | 10·34 | 10·36 | 10·39 | 10·42 | 10·45 |
| 12 | 11·21 | 11·24 | 11·27 | 11·30 | 11·34 | 11·37 | 11·40 |
| 13 | 12·14 | 12·18 | 12·21 | 12·24 | 12·28 | 12·31 | 12·35 |
| 14 | 13·08 | 13·12 | 13·16 | 13·19 | 13·23 | 13·26 | 13·30 |
| 15 | 14·02 | 14·06 | 14·10 | 14·13 | 14·17 | 14·21 | 14·25 |
| 16 | 14·95 | 14·99 | 15·03 | 15·07 | 15·11 | 15·15 | 15·20 |
| 17 | 15·88 | 15·93 | 15·98 | 16·02 | 16·06 | 16·10 | 16·15 |
| 18 | 16·82 | 16·87 | 16·92 | 16·96 | 17·01 | 17·05 | 17·10 |
| 19 | 17·76 | 17·81 | 17·86 | 17·90 | 17·95 | 18·00 | 18·05 |
| 20 | 18·68 | 18·74 | 18·79 | 18·84 | 18·90 | 18·95 | 19·00 |
| 21 | 19·62 | 19·68 | 19·73 | 19·78 | 19·84 | 19·90 | 19·95 |
| 22 | 20·55 | 20·61 | 20·67 | 20·72 | 20·78 | 20·84 | 20·90 |
| 23 | 21·49 | 21·55 | 21·61 | 21·66 | 21·73 | 21·79 | 21·85 |
| 24 | 22·43 | 22·49 | 22·55 | 22·61 | 22·68 | 22·74 | 22·80 |
| 25 | 23·35 | 23·42 | 23·49 | 23·55 | 23·62 | 23·69 | 23·75 |
| 26 | 24·29 | 24·36 | 24·43 | 24·50 | 24·57 | 24·64 | 24·70 |
| 27 | 25·23 | 25·30 | 25·37 | 25·44 | 25·51 | 25·58 | 25·65 |
| 28 | 26·16 | 26·23 | 26·20 | 26·37 | 26·45 | 26·53 | 26·60 |
| 29 | 27·10 | 27·17 | 27·14 | 27·31 | 27·40 | 27·48 | 27·55 |
| 30 | 28·03 | 28·10 | 28·18 | 28·26 | 28·34 | 28·42 | 28·50 |
| 31 | 28·97 | 29·04 | 29·12 | 29·20 | 29·29 | 29·37 | 29·45 |
| 32 | 29·90 | 29·98 | 30·06 | 30·14 | 30·23 | 30·32 | 30·40 |
| 33 | 30·83 | 30·91 | 31·00 | 31·08 | 31·17 | 31·26 | 31·35 |
| 34 | 31·70 | 31·85 | 31·94 | 32·03 | 32·12 | 32·21 | 32·30 |
| 35 | 32·71 | 32·79 | 32·88 | 32·97 | 33·07 | 33·16 | 33·25 |
| 36 | 33·64 | 33·73 | 33·82 | 33·91 | 34·01 | 34·10 | 34·20 |
| 37 | 34·57 | 34·66 | 34·76 | 34·86 | 34·96 | 35·05 | 35·15 |
| 38 | 35·50 | 35·60 | 35·70 | 35·80 | 35·90 | 36·00 | 36·10 |
| 39 | 36·44 | 36·54 | 36·64 | 36·74 | 36·85 | 36·95 | 37·05 |
| 40 | 37·38 | 37·48 | 37·58 | 37·68 | 37·79 | 37·89 | 38·00 |
| 41 | 38·31 | 38·41 | 38·52 | 38·62 | 38·74 | 38·84 | 38·95 |
| 42 | 39·23 | 39·35 | 39·46 | 39·57 | 39·69 | 39·79 | 39·90 |
| 43 | 40·18 | 40·29 | 40·40 | 40·51 | 40·62 | 40·73 | 40·85 |
| 44 | 41·11 | 41·22 | 41·34 | 41·44 | 41·56 | 41·68 | 41·80 |
| 45 | 42·05 | 42·16 | 42·28 | 42·39 | 42·52 | 42·63 | 42·75 |
| 46 | 42·98 | 43·10 | 43·22 | 43·34 | 43·46 | 43·58 | 43·70 |
| 47 | 43·91 | 44·03 | 44·15 | 44·27 | 44·40 | 44·52 | 44·65 |
| 48 | 44·84 | 44·96 | 45·09 | 45·22 | 45·35 | 45·47 | 45·60 |
| 49 | 45·78 | 45·91 | 46·04 | 46·17 | 46·30 | 46·42 | 46·55 |
| 50 | 46·72 | 46·85 | 46·97 | 47·11 | 47·24 | 47·36 | 47·50 |

*olumes of Gas read off to*

for temperatures between 0° a

| | 710 | 712 | 714 | 716 | 7…2 | 734 | 736 | 738 | |
|---|---|---|---|---|---|---|---|---|---|
| 51 | 47·65 | 47·79 | 47·92 | 48·05 | 48…2 | 49·26 | 49·39 | 49·52 | 4 |
| 52 | 48·58 | 48·72 | 48·85 | 48·99 | 49…8 | 50·22 | 50·36 | 50·49 | 5 |
| 53 | 49·52 | 49·66 | 49·79 | 49·93 | 50…5 | 51·19 | 51·33 | 51·46 | 5 |
| 54 | 50·45 | 50·59 | 50·73 | 50·87 | 51…1 | 52·16 | 52·30 | 52·44 | 5 |
| 55 | 51·38 | 51·53 | 51·67 | 51·82 | 51…8 | 53·13 | 53·27 | 53·41 | 5 |
| 56 | 52·32 | 52·47 | 52·61 | 52·76 | 52…4 | 54·09 | 54·23 | 54·37 | 5 |
| 57 | 53·25 | 53·41 | 53·55 | 53·70 | 53…0 | 55·05 | 55·20 | 55·35 | 5 |
| 58 | 54·19 | 54·34 | 54·49 | 54·64 | 54…6 | 56·02 | 56·17 | 56·32 | 5 |
| 59 | 55·13 | 55·28 | 55·43 | 55·59 | 55…3 | 56·99 | 57·14 | 57·29 | 5 |
| 60 | 56·07 | 56·22 | 56·37 | 56·53 | 56…79 | 57·95 | 58·10 | 58·26 | 5 |
| 61 | 57·00 | 57·15 | 57·31 | 57·47 | 57…75 | 58·91 | 59·07 | 59·23 | 5 |
| 62 | 57·93 | 58·09 | 58·25 | 58·41 | 5…72 | 59·88 | 60·04 | 60·20 | 6 |
| 63 | 58·87 | 59·03 | 59·19 | 59·35 | 5…68 | 60·85 | 61·01 | 61·17 | 6 |
| 64 | 59·80 | 59·96 | 60·13 | 60·30 | 6…64 | 61·81 | 61·98 | 62·15 | 6 |
| 65 | 60·74 | 60·90 | 61·07 | 61·24 | 6…60 | 62·77 | 62·94 | 63·11 | 6 |
| 66 | 61·67 | 61·84 | 62·01 | 62·18 | 6…57 | 63·74 | 63·91 | 64·08 | 6 |
| 67 | 62·60 | 62·77 | 62·95 | 63·12 | 6…53 | 64·71 | 64·88 | 65·05 | 6 |
| 68 | 63·54 | 63·71 | 63·89 | 64·06 | 6…50 | 65·68 | 65·85 | 66·02 | 6 |
| 69 | 64·47 | 64·65 | 64·83 | 65·01 | 6…45 | 66·64 | 66·82 | 67·00 | 6 |
| 70 | 65·40 | 65·58 | 65·77 | 65·95 | 6…42 | 67·61 | 67·79 | 67·97 | 6 |
| 71 | 66·34 | 66·52 | 66·71 | 66·89 | 6…39 | 68·58 | 68·76 | 68·94 | |
| 72 | 67·27 | 67·46 | 67·65 | 67·83 | 6…35 | 69·54 | 69·73 | 69·92 | |
| 73 | 68·20 | 68·39 | 68·58 | 68·77 | 6…31 | 70·51 | 70·69 | 70·88 | |
| 74 | 69·14 | 69·33 | 69·53 | 69·72 | 6…28 | 71·48 | 71·66 | 71·85 | |
| 75 | 70·07 | 70·27 | 70·47 | 70·66 | 7…24 | 72·44 | 72·63 | 72·82 | |
| 76 | 71·01 | 71·21 | 71·41 | 71·60 | 7…20 | 73·40 | 73·60 | 73·80 | |
| 77 | 71·94 | 72·14 | 72·34 | 72·54 | 7…17 | 74·37 | 74·57 | 74·77 | |
| 78 | 72·87 | 73·07 | 73·28 | 73·48 | 7…12 | 75·33 | 75·53 | 75·74 | |
| 79 | 73·80 | 74·01 | 74·22 | 74·42 | 7…09 | 76·30 | 76·50 | 76·71 | |
| 80 | 74·74 | 74·94 | 75·16 | 75·37 | 7…05 | 77·27 | 77·47 | 77·68 | |
| 81 | 75·67 | 75·88 | 76·10 | 76·31 | 7…02 | 78·23 | 78·44 | 78·65 | |
| 82 | 76·60 | 76·82 | 77·04 | 77·25 | 7…98 | 79·20 | 79·41 | 79·62 | |
| 83 | 77·54 | 77·76 | 77·98 | 78·19 | 7…94 | 80·16 | 80·38 | 80·60 | |
| 84 | 78·47 | 78·69 | 78·91 | 79·13 | 7…90 | 81·12 | 81·34 | 81·56 | |
| 85 | 79·41 | 79·63 | 79·86 | 80·08 | 8…87 | 82·10 | 82·31 | 82·53 | |
| 86 | 80·34 | 80·57 | 80·80 | 81·02 | 8…83 | 83·06 | 83·28 | 83·50 | |
| 87 | 81·28 | 81·50 | 81·74 | 81·96 | 8…79 | 84·02 | 84·25 | 84·48 | |
| 88 | 82·21 | 82·44 | 82·68 | 82·90 | 8…76 | 85·00 | 85·22 | 85·45 | |
| 89 | 83·15 | 83·38 | 83·62 | 83·85 | 8…72 | 85·96 | 86·19 | 86·42 | |
| 90 | 84·09 | 84·31 | 84·56 | 84·79 | 8…68 | 86·93 | 87·16 | 87·39 | |
| 91 | 85·02 | 85·25 | 85·50 | 85·73 | 8…65 | 87·89 | 88·12 | 88·36 | |
| 92 | 85·95 | 86·19 | 86·44 | 86·68 | 8…61 | 88·86 | 89·09 | 89·33 | |
| 93 | 86·87 | 87·12 | 87·38 | 87·62 | 9…57 | 89·82 | 90·06 | 90·30 | |
| 94 | 87·82 | 88·06 | 88·32 | 88·56 | 9…54 | 90·79 | 91·03 | 91·27 | |
| 95 | 88·76 | 89·01 | 89·26 | 89·50 | …50 | 91·75 | 92·00 | 92·25 | |
| 96 | 89·69 | 89·94 | 90·20 | 90·45 | …46 | 92·72 | 92·97 | 93·22 | |
| 97 | 90·62 | 90·87 | 91·13 | 91·38 | …43 | 93·68 | 93·93 | 94·19 | |
| 98 | 91·56 | 91·82 | 92·07 | 92·33 | …39 | 94·65 | 94·90 | 95·16 | |
| 99 | 92·49 | 92·75 | 93·01 | 93·26 | …35 | 95·61 | 95·87 | 96·13 | |
| 100 | 93·42 | 93·68 | 93·95 | 94·21 | …32 | 96·58 | 96·84 | 97·11 | |

(about 5 cub. centims.) of strong pure sulphuric acid for rinsing out the funnel. The evolution of gas is at first slow, especially if nitric acid is present. It is very much hastened by inclining the tube several times almost to the horizontal line, and quickly placing it upright again, so that the mercury falls through the acid.

In order to ascertain whether the acid in the measuring-tube has been exactly compensated by a higher level of the mercury in the side tube, the cock is opened after reading off. If the level of the acid rises, there has been too much pressure, and *vice versâ.* Consequently the change taking place after opening the cock is the opposite of what the correction of the reading should be. *E.g.*, if the reading was 15·3, but on opening the cock the acid rises to 15·2, the true reading would have been 15·4*.

To p. 76. *Exportation of brimstone from Sicily.*—This reached in 1877 the highest known figure, viz. 231,743 tons, 51,818 of which were sent to England, 38,440 to France, 42,589 to America, 98,896 to Italy and other countries. The price has fallen to from £4 5*s.* to £4 15*s.*; so that in some places it does not pay to get it.

To p. 79. *New occurrences of brimstone.*—At Pschow and Kokoschütz, near Ratibor, in Upper Silesia, beds of chalk marl full of reguline sulphur, up to 20 feet thickness, have been found (Chemische Industrie, ii. p. 136).

At Chillan in Chili, beds of sulphur have been discovered of such purity that it need only be ground and sifted to be ready for the market.

The sulphur-deposits at Guldbringe Syssel, in the south-west of Iceland, are stated to be actively worked with satisfactory results (Chem. News, xl. p. 31).

A new era began for sulphur in 1850–53, when it was recognized as the best means for combating the disease of the vine (*Oïdium*); but a considerable rise of its price was prevented by the contemporaneous introduction of pyrites for vitriol-making. The *refining* of brimstone is carried on most extensively at Marseilles, where about 17000 tons per annum are imported, and partly manufactured into flowers of sulphur, partly into roll sulphur, partly merely ground to powder. The flowers are used for the *Oïdium*, for vulcanizing india-rubber, etc.; roll-sulphur for

* Not all "nitrometers" found in the trade are of convenient construction. That which is described in the text (and sold by Mawson and Swan, of Newcastle-upon-Tyne) is in use at most German sulphuric acid-works.

gunpowder, lucifer-matches, ultramarine, carbon disulphide, pharmaceutical preparations, bleaching of straw, wool, etc. Ground crude brimstone is also largely used against the *Oïdium*; but it is very inferior to flowers, because the latter are much purer, much finer, and adhere better to the vines.

Since 1860 the Italian and Belgian refineries have been in severe competition with those in the south of France; this has driven the latter to introduce great improvements in the manufacture. Before 1860 the loss of sulphur in refining was 15 to 16 per cent.; now it is only 3 to 4 per cent. The consumption of fuel, formerly 35 to 40 kg. per 100 sulphur, is now no more than 25 kg.

*Ground sulphur*, even its better qualities, is a heavy sandy powder. *Flowers of sulphur*, however, form a loose, flocculent, light powder, consisting of minute globules united in botryoidal masses; they consequently adhere better to the vines, and offer more resistance to the wind and the rain.

To p. 81. *Extraction of Sulphur from pyrites, &c.*—Gerlach (Dingl. Journ. ccxxx. p. 61) gave more explicit information on his patent process for extracting sulphur from ores and other materials containing it by means of superheated steam. The ores, &c., are brought to or beyond the melting-point of sulphur in iron or clay retorts, or in suitable furnaces; and superheated steam is passed over them. The latter is brought to a red heat in a long wrought-iron tube melted into a block of cast-iron. It carries over the sulphur-vapour very quickly into a receiver filled with water. This process is also applicable to sulphurous marls; and it is especially adapted to spent oxides of gasworks contaminated by tar, from which by that process pure yellow brimstone can be obtained—the extraction by means of carbon bisulphide, formerly practised by the gas-works at Stratford, near London, having had to be given up again, owing to the trouble caused by the tar. Neither is a percentage of iron filings and sawdust in the spent oxides injurious in this process, whilst it is very so when the mass is employed in the manufacture of sulphuric acid. It is preferable to levigate the mass first, separating the heavier iron oxide (which can be used over again for the purification of gas) from a lighter mass, containing 70 per cent. of sulphur, which is submitted to the distilling process. Some further details and sketches referring to this process are found in the Chemiker-Zeitung, 1879,

p. 593. A process in every respect resembling Gerlach's has been patented by O. C. D. Ross (No. 713, Feb. 21, 1879).

A similar process is described in the 'Scientific American,' xxxix. p. 276. A current of superheated steam is to be passed over pyrites heated to a dark red in a retort; half of the sulphur is carried away by the steam; at the same time more or less sulphuretted hydrogen escapes, according to the temperature and the duration of the process. For the production of brimstone a temperature of 870° C. [?] and upwards is most favourable. At 815° cupreous pyrites of 47·96 per cent. yields 23·07 per cent. brimstone; the remainder escapes almost entirely as $H_2S$. The distilled sulphur is purified from arsenic by treating it with alkali or sodium sulphide at the ordinary temperature. From the residue, by the action of air and moisture, cupric sulphate, and from this metallic copper may be obtained.

*Holloway's process* (patented, No. 500, Feb. 6, 1878) has recently caused a great stir. In this the heat produced by the combustion of one portion of the pyrites is utilized for decomposing the remainder into a matt or regulus and distilled sulphur. If heated air is blown through a batch of melted iron sulphide, the process can be carried on continuously; more pyrites, along with sandstone as a flux, is regularly charged; and the slag, along with a cupreous regulus, is tapped off. The current of air must be regulated so that oxygen is never in excess. This process aims more particularly at concentrating, in a cheap manner, the copper of poor ores in countries where fuel is expensive, so as to cheapen the carriage to the countries where the copper can be smelted. Some idea is also entertained of utilizing the $SO_2$ given out for the production of vitriol. Thus far the process is still in the experimental stage. A pamphlet, published by the inventor, contains a detailed report of the results hitherto obtained (from a paper read before the Society of Arts), and the discussion which followed the reading of the paper. A critical report upon the same was given by Bode in Dingler's Journal, ccxxxii. p. 433. Dr. Smith (Inspector's Report, 1877–78, p. 47) seems to expect important results from it.

To p. 82. *Employment of pyrites for vitriol-making in America.* —An occasional remark made by Du Puy (Chem. News, xxxix. p. 36) shows that pyrites is actually employed for vitriol-making at the New-Jersey Chemical Works.

To p. 97. *Norwegian pyrites.*—There is a large mine of cupreous pyrites, with 45 per cent. sulphur and 3 per cent. copper, at Vigsnaes, worked by an Antwerp company. It is described by Kuhlmann fils in the Mémoires de la Société industrielle du Nord de la France, 1874.

To p. 105. *Estimation of sulphur in pyrites.*—Fresenius (Zeitschr. f. anal. Chemie, xix. p. 53) maintains that the dry way of resolving pyrites is preferable to the wet one, because in the former way the iron does not enter into solution; this prevents a double error in the estimation of sulphur, as $BaSO_4$ is soluble to some extent in an acid solution of ferric chloride, and as it is next to impossible to obtain the precipitate free from iron in such a solution. Although these two errors are opposite to each other, the result is that the dry assay yields about 1 per cent. more sulphur in pyrites than the wet. The author has, however (in a paper published in the same journal), shown that this difference is principally caused by the circumstance that in the wet assay the sulphur of gypsum, barytes, and galena is not estimated, or at least only partly, which is far from being a drawback of the process. The errors pointed out by Fresenius are very slight, and so far compensate each other that the final error is less than the differences between the check analyses quoted by Fresenius himself; it can, moreover, be entirely avoided by precipitating the iron by ammonia, and estimating the sulphuric acid in the filtrate.

To p. 106. *Estimation of sulphuric acid in the volumetrical way* (Wildenstein's process).—According to Haddock (Chem. News, xxxix. p. 156) it is much easier to recognize a slight precipitate in the drops of barium chloride if they are not placed (as usual) on a glass plate with dark background, but upon a mirror. In this case the slightest precipitate is very clearly visible; nor does it matter whether the liquid is coloured or not.

To p. 112. *The damage caused by acid vapours to vegetation* has been discussed in a long paper by Hasenclever (Chem. Industrie, 1879, p. 225), who points out how much damage is done by coal-smoke alone. König (Dingler's Journal, ccxxix. p. 299) describes the appearance of trees destroyed by the vapours from roasting blende. Hasenclever, in the above paper, gives coloured and photolithographic illustrations of the ravages caused by acid vapours and metallic sulphates upon the leaves of plants and plantations of trees, side by side with those owing to frost, autumnal

decay, fungi, drought, overgrowth of other trees, &c. The effects of these causes are often wrongly ascribed to the acid vapours from chemical works. Neither is the estimation of sulphates and chlorides in the damaged leaves &c. at all a safe guide to the detection of the real cause. He especially points out the enormous quantity of acid vapours unavoidably sent into the air wherever coal is consumed, which is very much larger than that emitted by chemical works. A remedy against this has been sought for in tall chimneys; but these cannot do any real good, except in the case of small and isolated works. The very considerable nuisance caused by the calcining of sulphurous ores (such as copper pyrites, blende, &c.) has been immensely reduced by proper apparatus for condensing the $SO_2$ into sulphuric acid, but has not been entirely suppressed. The condensation of hydrochloric acid (which formerly was one of the worst nuisances) has now become so perfect, at least in Germany (where that acid has ceased to be an incumbrance, and become a profit to the manufacturer), that any special legislation was thought unnecessary by the Government, although the matter had been under consideration. What an insignificant part is now played by the escape of noxious gases from chemical works, in comparison with that from other sources, is proved by a communication from Mr. Fletcher, referring to the acids escaping at St. Helens. These are calculated,

| | | | | |
|---|---|---|---|---|
| From | fire-gases, | at 800 | tons | per week. |
| ,, | copper-works, | ,, 380 | ,, | ,, |
| ,, | glass-works, | ,, 180 | ,, | ,, |
| ,, | alkali-works, | ,, 25 | ,, | ,, |

At Stolberg, near Aachen, where, on a superficial area of 1600 acres, 220 chimneys emit 34500 kilog. of $SO_2$ from coal, and 50858 kilogs. of $SO_2$ from zinc-works, glass-works, &c., the alkali-works only add 480 kilog. $SO_2$ and 750 kilogr. HCl, =4 per cent. of the total acids. Consequently alkali-makers ought not to be blamed for the total or the chief part of the damage seen to have occurred in the neighbourhood.

*For condensing the sulphurous acid formed in refining sulphur* several processes have been recently proposed. According to the 'Moniteur des Prod. chim. et de la Droguerie,' viii. p. 242, the condensing-chambers for sulphur are connected with the

chimney by means of pipes starting from their lower portion, with the interposition of a condenser containing sodium carbonate and lime.

A German patent of the Society Pilter at Paris (No. 2661, July 23, 1877) proposes employing the sulphurous acid for treating natural phosphates under the pressure produced by the evolution of carbonic acid from the carbonates contained in the mineral. In this case the calcium triphosphate is converted into calcium monophosphate and calcium sulphite. The latter is separated from the solution of the former by crystallization and centrifugal force. The calcium monophosphate is either thickened by an addition of gypsum and sold as superphosphate; or calcium biphosphate is precipitated from it by lime, or it is worked up for phosphorus.

According to the 'Polyt. Notizblatt,' 1878, p. 384, Mr. Schnabel, manager of the Lautenthal smelting-works, has succeeded in resolving certain weathered clay slates, moistened with water, by gases containing sulphurous acid. This was formerly only done with alum slates proper. The aluminium sulphate formed is obtained by lixiviation.

At some zinc-works the fumes from calcining blende are absorbed by passing them through towers fed with a shower of milk of lime, or through cisterns in which a spray of milk of lime is produced by paddle-wheels, or chambers filled with limestone and kept constantly wet by a jet of water.

A patent of Allen's (No. 189, Jan. 16, 1879) aims at a real utilization of dilute sulphurous gas, *e.g.* that produced in Hollway's process (p. 341), by causing it to be absorbed by freshly-ignited wood-charcoal, and reexpelling the $SO_2$ by exhausting the air, etc.

A German patent of Hartmann's (No. 9275, 1879) seeks to utilize $SO_2$ by passing the gases, mixed with steam, over red-hot coke, or, mixed with petroleum vapour, over any red-hot materials, in order to convert it into $H_2S$, where the latter gas is intended to be employed.

A very important report, by Dr. Bernouilli, on the Upper-Silesian zinc-works (p. 153 of the Official Government report), proves that even in calcining blende the nuisance caused by $SO_2$ can be adequately abated. In the Reckehütte, at Rosdzin, blende with 25 per cent. sulphur is calcined; the lumps are burnt in

ordinary kilns down to 8 per cent., the smalls in Hasenclever furnaces (comp. Vol. I. p. 202) down to 10 per cent. of sulphur; and the escaping gases are conveyed into vitriol-chambers, where 15 tons of sulphuric acid are turned out per diem. The burnt ores are deprived of the remaining sulphur in reverberatory furnaces; and the gases from these are conveyed, first into flue-dust chambers, and from these into brick towers, where they meet a shower of milk of lime. The latter is divided into small jets by a packing of fireclay pieces of this shape (⌐¬); at the bottom it arrives partly converted into calcium sulphite and sulphate. The milky liquid runs into settlers, from which the clear water can run away without any nuisance; the deposit contains on an average (in the dry state) 33·5 per cent. calcium sulphite and 6·5 calcium sulphate. As the remainder consists of calcium hydrate and carbonate, it is used over again, till these are also saturated; and finally the mixture is employed as manure, in the absence of any better application. The plant, including the flue-dust chambers, cost £175; the expenses of the process amount to £17 per month, principally for lime (45 tons) and labour (66 working-days). The official inspection showed a diminution of $SO_2$ from 0·258 per cent. by volume in the entering gas to 0·017 per cent. in the exit gas, *i. e.* an absorption of 93·4 per cent. of the total $SO_2$. When the supply of milk of lime was very good, not even traces of $SO_2$ could be found in the exit-gas.

A German patent by M. Freytag (No. 9969, Nov. 11, 1879) proposes absorbing the sulphuric acid in the gases from calcining zinc, lead, or copper ores by passing them through coke condensers fed with a stream of sulphuric acid itself.

A very careful investigation on the removal of small quantities of $SO_2$ from the smoke of ultramarine works was carried on for ten years by Cl. Winkler, at the Bockau works in Saxony. An attempt to absorb the $SO_2$ by nitrous vitriol did not succeed to a sufficient extent, owing to the great dilution of the gas. More success was obtained by the following somewhat complicated method. Sodium sulphate was formed by igniting sulphate with 25 to 30 per cent. small coal in furnaces, the hearth of each of which was made of a single block of marble, and protecting the fluxed mass from the contact of air; it was afterwards found more suitable to make the $Na_2S$ by decomposing $Na_2SO_4$ with BaS, the latter being prepared by igniting barium sulphate with coal in crucibles, of which 495 were placed in a furnace. The $BaSO_4$ formed in the process was

always reduced over again. The solution of $Na_2S$, trickling down in a tower, was employed for absorbing the $SO_2$ in the gases ascending in the tower. It was expected that sodium hyposulphite would be formed; but, owing to the temperature rising to 40°, it was found that, instead of this, sodium tetrathionate was formed:

$$Na_2S + 3SO_2 = Na_2S_4O_6.$$

On heating this solution, the salt decomposes, thus:

$$Na_2S_4O_6 = Na_2SO_4 + SO_2 + 2S.$$

The sulphur was obtained in the solid state, the $SO_2$ conveyed back into the absorbing-tower, and the $Na_2SO_4$ employed over again to form $Na_2S$. Of course subsidiary reactions take place as well, and the process is much too complicated to be carried on without constant supervision by a chemist. Owing to this the process was ultimately abandoned, and the absorption of the $SO_2$ effected by passing the gases through a series of chambers filled with limestone and constantly sprinkled with water, which removes the calcium sulphite and sulphate as they are formed. Whilst the gases on entering the chambers average 0·360 per cent. $SO_2$ by volume, the average percentage on leaving is only 0·039 $SO_2$—an extraordinarily favourable result.

To p. 113. *Treatment of blende for obtaining sulphur therefrom.*—German patent, application No. 23280, Nov. 30, 1878. The blende is partially calcined, so that a mixture of ZnO and ZnS results; this is heated with quicklime and coal or coke in a muffle, zinc distilling and calcium sulphide remaining behind. The latter is treated with hydrochloric acid; the $H_2S$ escaping is mixed with the $SO_2$ given off in the partial roasting of the blende; and in this way sulphur is precipitated.

To p. 121. *Occurrence and manufacture of nitrate of soda.*—Further detailed statements on these points have been made by Langbein in Dingler's 'Journal,' ccxxxii. p. 453, and in Wagner's 'Jahresbericht,' 1879, p. 380.

To p. 126. *Nitric acid.*—In the ordinary cylinders at first the fire is pushed on strongly; but as soon as the first receivers get warm the fire is slackened, and during 18 hours is kept so that of eight receivers only the first five are warm to the touch. If the heat gets up too high, the contents of the retort may boil over. The end of the reaction is known by the cooling of the receivers; then the fire is increased again for a little time, and at last is allowed to go down.

At Griesheim the ends of the cylindrical retorts are protected by stone flags from cooling too much. The system (described in the text) of pots quite surrounded by the fire has been discarded there, because the emptying of those pots is very troublesome, and pots with a side branch for running out the residue cannot be made to stand long.

Cooling by worms or Goebel's tubes has been found to require too much care and labour; so that the ordinary receivers are employed as before; but there is certainly a considerable breakage of them.

At another German works, stoneware worms have been found to answer very well indeed, if properly manufactured. They admit of convenient "fractionating," and save the somewhat dangerous emptying of the receivers.

The following are *cost accounts* for nitric acid from real work at a Swiss factory:—

1. *For acid of* 36° *Baumé* (=sp. gr. 1·334 or 50 per cent. $NO_3H$).

| | frs. |
|---|---|
| 4 charges of 4 cwt. nitrate of soda at 20 frs.... | 320 |
| 16 cwt. sulphuric acid 144° Tw., at 3½ frs. ... | 56 |
| 10 cwt. inferior lignite (brown coal), at 0·9 fr. | 9 |
| 2 men, at 3½ frs. .................................. | 7 |
| Interest and amortization ........................ | 10 |
| General expenses .................................. | 2 |
| Packages, etc. ..................................... | 70 |
| Yield: 21 cwt. nitric acid of 36° Baumé ...... | 474 |
| 1 " " " ............... | 45·14 |
| | (say £1 16*s*.). |

2. *For nitric acid* 50° Bé. (=sp. gr. 1·532=93 per cent. $NO_3H$).

| | frs. |
|---|---|
| 6 cwt. nitrate of soda, at 24 frs. ............... | 144 |
| 6 cwt. sulphuric acid 170° Tw., at 8 fr. ...... | 48 |
| 6 cwt. inferior lignite, at 0·9 fr. .............. | 5·40 |
| Wages ................................................ | 6 |
| Sundries and general expenses ................. | 15 |
| Small stores ........................................ | 14 |
| Yield 3 cwt. 2 qrs. 10 lbs. acid .................. | 232·40 |
| Deduct 5 cwt. nitre cake, at 4 frs. ...... | 20 |
| | 212·40 |

1 cwt. nitric acid of 50° Baumé... 59 frs.
(say £2 7*s*.).

(N.B. Packages are not included in this second calculation, nor yet interest and amortization.

To p. 145. *Improved Sulphur-burner.*—A modification of the principle which is employed both in Blair's burner and in that shown in figs. 16–19, viz. burning the sublimed sulphur by introducing air into a chamber where it can deposit before the burner-gas reaches the chambers, was patented by H. Glover in 1879 (No. 3774). The main feature of this invention is that the subliming-chamber is loosely packed with bricks, and is allowed to be filled with sulphur and burnt out alternately.

To p. 150. *Stone-breakers.*—Several new systems have recently been introduced. Durand and Chaptal's consists of a number of hammers attached to a horizontal revolving shaft. It is said to make less dust than other stone-breakers. The smallest apparatus breaks from 8 to 25 tons of stone in 10 hours, with an expenditure of 2 or 3 horse-powers, the larger size from 80 to 130 tons, with 6 horse-powers.

Vapart's breaking-mill (address, "Chênée, Vieille Montagne") works with centrifugal force.

The Humboldt Engineering Company at Cologne (Germ. Pat. 1906, Jan. 12, 1878) manufacture stone-breakers which do twice the work of those formerly in use, with the expenditure of the same force.

Other improvements in stone-breakers have been invented by Brown (Scientific American, 1879, p. 194) and Welter (German patent, No. 7494, March 5, 1879).

To pp. 165 & 179. *Discharging of burnt pyrites from the burners.*—This ought to be done as quickly as possible, and is sometimes expedited by iron bogies running on tramways, which are introduced into the ash-pits, and into which the cinders fall as the grates are shaken. This very suitable plan necessitates a system of tramways and turn-tables, as well as a lowering of the whole floor. The following simple and equally efficient plan seems, therefore, worthy of recommendation. It is a tilting-box, which the author has seen at the Munich gas-works, figs. 110 & 111. There are two independent parts :—first, an iron box, of suitable dimensions, with two outside pivots near the upper edge ; secondly,

a light but strong wheeled frame, which ends in forks fitting under those pivots. As shown in the diagram, the whole is used in the

Fig. 110.

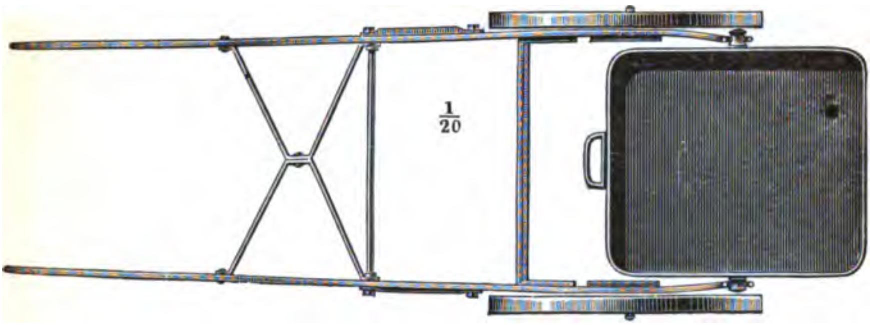
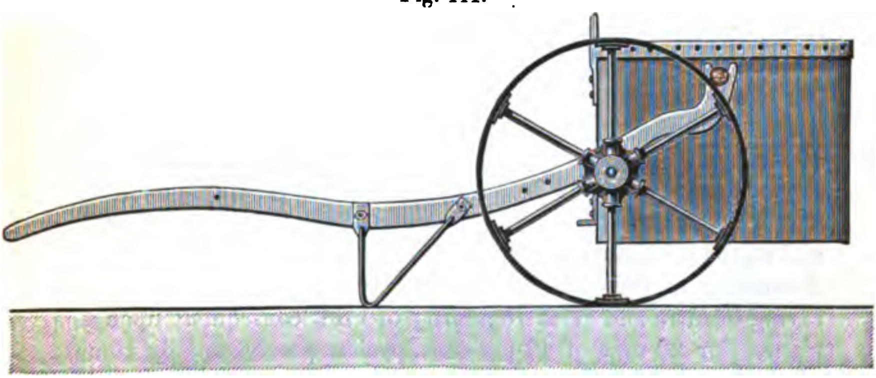



Fig. 111.



manner of an ordinary iron wheelbarrow on any hard ground. But by lifting up the handle the box is first lowered to the ground, then the forks slip out and the frame can be run back. Similarly the box is taken up again by running the frame in, and depressing the handles till the forks take hold of the pivots. The boxes can be made to fit into the ash-pits, and the cinders discharged into them directly from the grates. Of course other applications of this barrow will present themselves in chemical works.

To p. 177. *Regulation of air and prevention of scars.*—At the Griesheim chemical works I found that no scars are ever formed.

Although all the burners belonging to one set of chambers are only separated by low partitions, and communicate with a wide gas-space, they do not admit of individual regulation of the draught either at top or bottom, the only regulation taking place in the exit-pipe from the Gay-Lussac column. But the above favorable result is attained by carefully separating the ore (which is crushed by a Blake's stone-breaker) into lumps, peas, and dust. Only 75 per cent. of the ore (Rio-Tinto pyrites) is burned in the lump-burners, and lies therein 19½ inches deep; the draught being never obstructed by smaller pieces, no scars are ever formed, and no more than 1½ per cent. of sulphur remains in the cinders. The peas and dust are burnt, each kind separately, in shelf burners very similar to Schaffner's (Vol. I. p. 219). By this careful separation of the ore according to size the burning-process has been extremely simplified, and gives next to no trouble.

To p. 179. *Prevention of the Entrance of Air and the Blowing-out of Gas during the Discharging of the Ash-pits of Pyrites-burners.* —Norrington (pat. No. 4131, Oct. 17, 1878) makes the ash-pit doors to slide in horizontal frames, and connects all the doors of a set of burners by jointed rods, so that they can be all moved together in a horizontal plane by means of an endless screw and gearing placed at one end. All the ash-pit doors are thus opened and shut at the same time in about ¼ minute. The latter is always done whenever any one of the working-doors is opened for charging etc.; and as the air cannot enter in any other way, no gas can blow out. According to information furnished by the inventor, there is a saving of nitre and great regularity of work consequent upon this plan. For 20 tons of 49-per-cent. pyrites per week, only 10 cwt. of nitrate of soda are consumed, or, if 64 tons of ore are burnt in the same kilns, 1¼ lb. of nitrate per cwt. of ore. The sulphur in the burnt ore is rather under 2½ per cent. According to the latest communications received from Messrs. Charles Norrington and Co., Plymouth, the consumption of nitrate is below 2 per cent. on the sulphur, and the production equal to 3 tons of oil of vitriol for every ton of sulphur burnt. (This probably means so-called acid of 170° Tw., not real $SO_4H_2$.)

They also state that the saving from the suppression of the loss of nitre- and sulphur-gases at the time of charging the kilns is about £5 per kiln per annum, and that, owing to the regularity of the amount of draught admitted to each kiln, they all burn

quite equally, whilst formerly some were always hot and others sluggish.

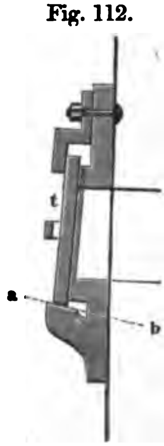
To p. 192. *Burning pyrites smalls by means of the heat from a burner for lumps* was first carried out in a furnace constructed by Usiglio and Dony, and patented in France Jan. 24, 1852.

To p. 214. *Gerstenhöfer's pyrites-burner,* according to the most recent and trustworthy information, seems well adapted to ores or metallurgical products containing from 25 to 36 per cent. sulphur. Below 25 per cent. it does not work; above 36 per cent. it is inferior to the shelf burners (p. 215).

To p. 215. *Invention of the shelf burners.*—This, as the author has learned from an authentic source, is not due to M. Juhel, but to M. Malétra himself and M. Tinel. At the Rouen works the sulphur is now burnt down to 0·5 per cent. in the cinders.

To p. 215. *Burner for Pyrites Smalls.*—Mactear has patented (No. 3901, Sept. 19, 1878) an apparatus quite similar in principle to the shelf burners described in the text. The shelves are slightly inclined; and there are a few other deviations from the plan which has been found to answer so well on the Continent; but it is not clear that any thing is gained by these alterations of the original shelf burner, which latter, not having been patented, is common property.

Fig. 112.




To p. 219. *Doors of the shelf burners.*—The diagram (fig. 84) is not quite correct; fig. 112 gives a more correct one. The door *t* is in a slanting position, and moves on the planed ledge *a b*.

To p. 225. *A mechanical pyrites-burner* was patented by Farmer and Hardwicke in 1878. It is of circular section, 18 feet wide, and has four shafts, to which stirrers are attached at various distances, so that the pyrites is turned round in all directions. The burner (which is in principle very like Jones and Walsh's salt-cake furnace) is automatically charged and emptied. 5½ tons of pyrites are charged at a time, and burnt off in from 7 to 9 hours. One ton of coals is said to be sufficient for burning 18 tons of pyrites, and much labour is saved in comparison with ordinary burners. (The author has not been able to ascertain the practical success of these burners.)

To p. 230. *Spent oxides of gas-works* cannot be burnt in Gerstenhöfer kilns by themselves, because the melting sulphur stops up the feeding-rolls. They are sometimes moulded into bricks and put into lump-burners, where they burn off very well; but the grate-bars should be touched as little as possible, and the cinders must be allowed to fall through by themselves. It is preferable to employ shelf burners for this purpose.

To p. 247. *Estimation of sulphur dioxide in burner-gas by Reich's process.*—According to Cl. Winkler's 'Analyse der Industriegase,' ii. p. 350, it is better to employ a smaller absorbing-vessel, since the reaction is sharper in a smaller bulk of liquid. An addition of ammonium carbonate, or, still better, of sodium carbonate, to the iodine solution is very advantageous, and prevents any loss of $SO_2$ in a rapid current of gas. For approximate estimations an indiarubber finger-pump will do.

To p. 254. *Estimation of oxygen in chamber-gas.*—Phosphorus is again recommended by Lindemann (Zeitschr. f. analyt. Chemie, xviii. p. 158), who employs it in very thin sticks, in a pipette luted by water, quite analogous to Orsat's apparatus. The advantage of phosphorus is that it goes on much longer without renewal than pyrogallic acid.

M. Liebig (Dingl. Journ. ccxxxiii. p. 396) also describes some new apparatus for technical gas-analysis.

To p. 258. *Cooling of the draught-pipes from the pyrites-burners.*—The lead pipes with water-jackets, mentioned in the text, have been abolished in some of the places where they were erected, and have been replaced by metal pipes, which, if long enough, cool the gas down to 29° C. They stand very well if made from white cast iron. They are preferable to lead pipes, because the latter require a good deal of water for cooling, and are often needing repair.

To p. 260. *Flue-dust from pyrites-kilns.*—D. Playfair (Chem. News, xxxix. p. 245) claims to have found in such (from Spanish pyrites) 0·002 per cent. of thallium, and in the residue insoluble in sulphuric acid 0·002 per cent. of tellurium and 0·001 per cent. of selenium.

To p. 273. *Erection of lead chambers.*—At Griesheim (where each set consists of one very large chamber, 260 × 33 × 20 feet, combined with a small back chamber) the chambers are erected in a peculiar manner. On a staging of the whole area of the chamber-

bottom, but raised above its top, first the ends are made, then the sides, last of all the top, so that ultimately five sheets of lead are lying one above another. Then the top-straps are burnt on and joined to the top-joists, which are put in their places. Now the whole is supported on six differential pulleys, and the staging is removed. As this is done the ends and sides drop down into their places, and need only be joined in the corners, where they are bent in at an obtuse angle. Thus, as will be seen, nearly all the burning is horizontal, and the work is done more quickly, cheaply, and substantially.

To pp. 283, 284, 287. *Shape of acid-chambers &c.*—M. Delplace (communication to the author) has also found, by experience with many sets of chambers, that the shape of the chambers has practically no influence on the amount of work done in them; the cubic contents are the only consideration. He prefers wide chambers to long and narrow ones, as easier to regulate; they are less influenced by the oscillations of the process than the narrow chambers, because the entering gases get better mixed up with those already in the chamber. To assist this, he fixes the entrance-pipe more to one side of one of the gable ends. A single long chamber of 105,000 cubic feet yielded exactly as much vitriol and consumed just as little nitre as a set of several small chambers.

To p. 289. *Glass partitions in lead chambers* are not stable, unless the lead hooks for hanging the sheets of glass are *cast*; if made of sheet lead, they are too weak, and easily bend. These partitions have quite recently been done away with at the Uetikon works, where they were mentioned in the text as existing.

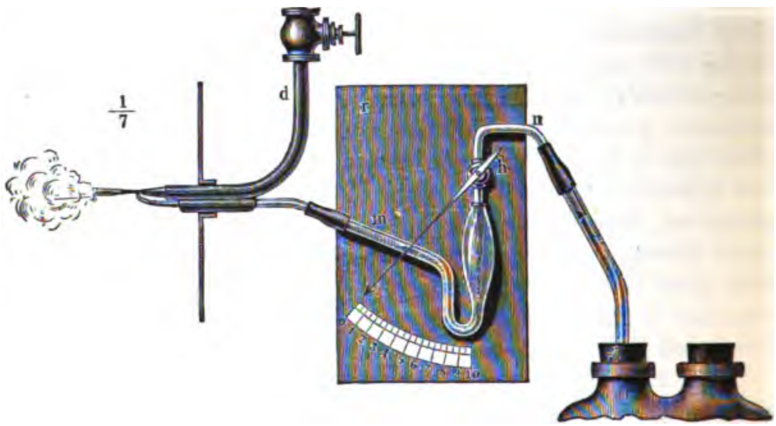
To p. 296. *Drawing off the acid.*—The simplest plan is to dispense with all plugs, siphons, &c., and to close the hole in the side of the chamber (fig. 126, p. 297) by an indiarubber cork; this is done by hand, which the man must certainly dip into the acid for a moment.

To p. 299. *Setting a siphon in carboys.*—This is most simply done by putting the siphon into the carboy, and closing the top of this by a lump of clay, through which passes a short glass tube; by blowing into the latter the siphon is made to run. A pamphlet on siphons was published by M. de Hemptinne, at Brussels, in 1880.

To p. 318. *Introduction of nitric acid into the chambers.*—Liebig (Zeitschr. des Vereins deutsch. Ingen. 1879, p. 111) claims to have

effected a great improvement in this by means of a spray-apparatus, fig. 113, consisting of a lead steam-pipe *d*, with platinum nozzle, parallel to which runs a glass pipe *m*, for conveying the nitric acid, bent up in front and drawn out into a fine point. The steam rushing past this causes a vacuum in the glass tube, and sucks acid through the latter from a stock-bottle, a glass cock *h* regulating the supply. The acid is divided into a fine mist; and none of it arrives at the bottom undecomposed.

Fig. 113.

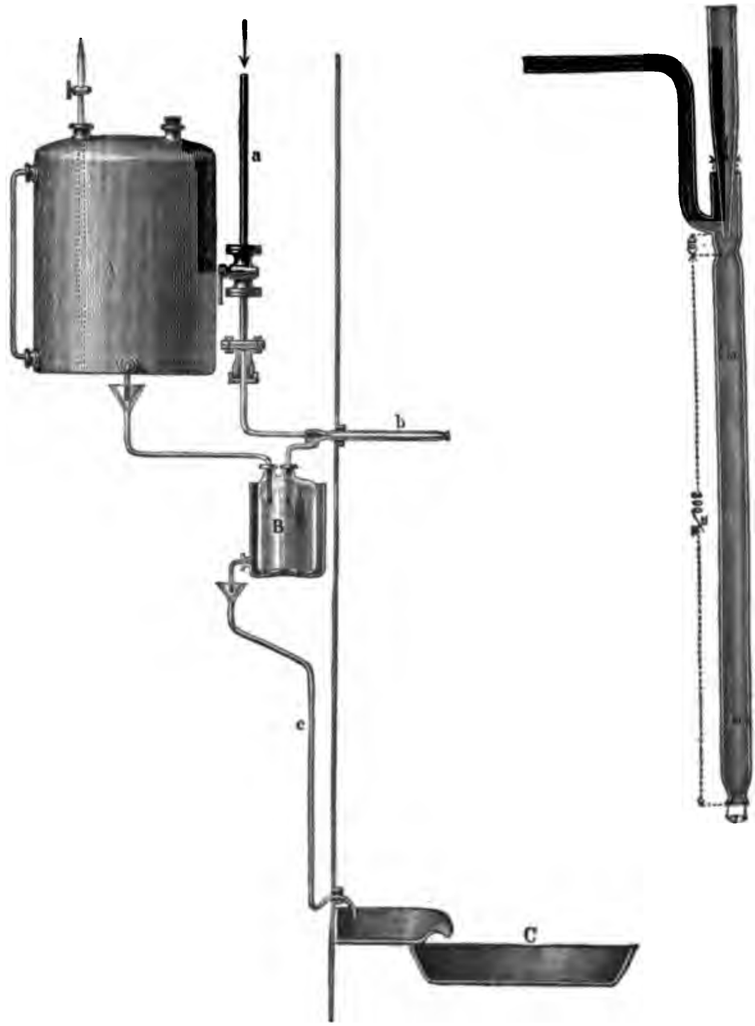



Another apparatus for the same purpose, constructed by Mr. Stroof, of the Griesheim works, has been communicated to the author by that gentleman, and is illustrated by figs. 114 and 115.

Fig. 114 shows the general disposition, fig. 115 the details of the injector *b*. The nitric acid runs from a Mariotte's bottle A into a Woulfe's bottle B, standing in a glass dish, provided with an overflow-pipe *c*, which conveys the acid, in case of the injector giving out, onto the cascade C. From the bottle B the acid is sucked away by the glass injector *b*, whose steam-jet is connected with the steam-pipe *a* by a stuffing-box. Such injectors are best made of well-annealed water-guage pipes, drawn out to a point. The point projects but loosely into the suction-pipe; so that a little air is sucked in as well, and no breakage can take place by expansion. At a pressure of 1½ atm. the injector can carry away 16 cwt. of nitric acid in 24 hours in the form of a spray, along with a little

air. The mouthpiece of the injector must be contracted and widened out again, like that of a fire-engine, to prevent any larger

Fig. 114. Fig. 115.




drops forming at that place. The acid is thus completely converted into a mist, and a sensible saving effected in comparison with cascades.

Another modification of a glass injector has been described by Burgemeister (Dingler's Journ. ccxxxv. p. 277).

To p. 319. *Introduction of nitrate of soda in solution.*—Blinckhorn (pat. No. 1084, March 10, 1878) runs such a solution of 70° Tw. in a regular jet upon sulphuric acid heated by the burner-gas. The solution of sulphate is drawn off from time to time.

To p. 327. *Water-spray for lead chambers.*—At Griesheim (where the price of fuel is very high) it has been found economical to entirely dispense with steam for feeding the chambers, apart from that supplied by the Glover tower, and introduce the water in the shape of sprays, but very differently from Sprengel's plan. The sprays are not produced by an injection of steam, but by allowing the water, at a pressure of 2 atmospheres, to issue from a small platinum jet against a platinum button (comp. Vol. II. p. 204). Two rows of such jets are introduced through lutes in the chamber-top, the jets about 20 feet apart. Thus the whole chamber is uniformly filled with a fine mist. The temperature of the gas entering from the Glover tower, which is sometimes as low as 35° C., rises to 50° C. where it meets the first jet, owing to the chemical action which takes place. It is certainly a drawback that all the water must be carefully filtered, as otherwise the jets would soon be stopped up; but this is more than compensated by the saving in fuel for steam.

To p. 330. *Regulation of the draught in the chambers.*—Especially in the case of chambers not connected with a high chimney, where changes of wind &c. produce great variations of draught, it is advisable to adopt some automatic regulation along with the ordinary dampers, &c. Such an automatic apparatus can be made by putting onto the horizontal part of the exit-pipe a perpendicular 12-inch pipe, closed by a bell standing in an annular water lute. The bell hangs on one arm of a lever, whose other arm is so weighted that the bell can travel freely. When the draught is just right, this second arm has a certain position, in which a throttle-valve within the exit-pipe connected with it is half open. When the draught increases, the bell descends, owing to the increase of atmospheric pressure, and partly shuts the throttle-valve; in the opposite case of the draught decreasing, the throttle-valve is opened wider. This apparatus, as constructed by M. Delplace, and employed by him for the last ten years with the greatest advantage, is shown in fig. 116, where *a* is the entrance-pipe from the Gay-

Lussac tower, *c* the exit-pipe, *b* a conical valve, *d* the regulating bell, *e e* the water-line of the hydraulic joint, *f* the lever, *g* the balance-weight.

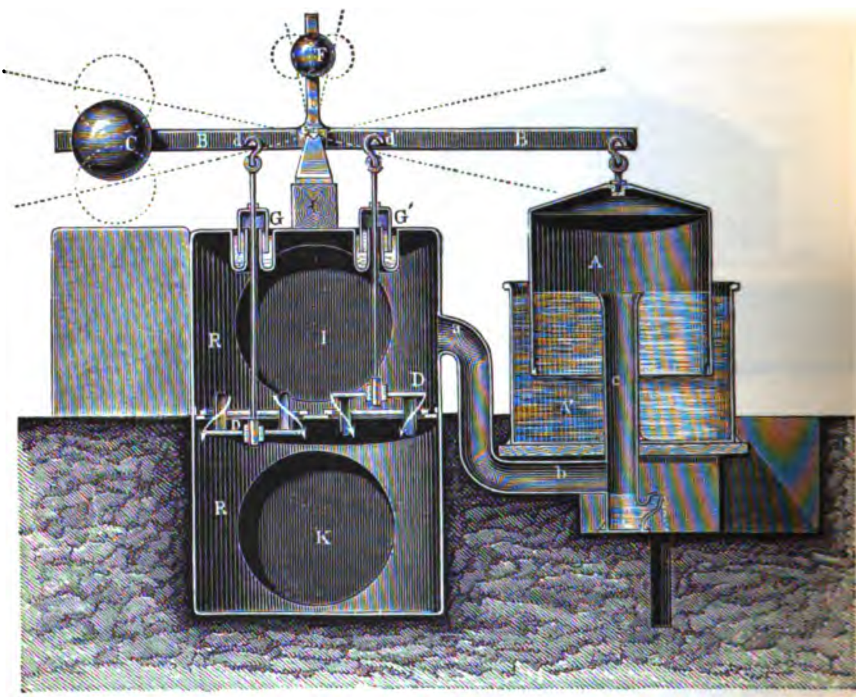
Fig. 116.

Somewhat different in detail, and apparently very accurately working, is the apparatus of Mr. W. G. Strype, of Wicklow, of which the following is a description (patent No. 705, Feb. 21st, 1879):—

The accompanying drawings illustrate two forms of the apparatus, fig. 117 being the most desirable, although somewhat more expensive in construction than the arrangement shown in fig. 118. Referring to fig. 117, an inverted vessel or receiver A, open at its lower end, dips into a tank $A^1$, containing water or other suitable liquid acting as a hydraulic joint. The interior of A is placed in communication, by means of the pipe or passage *a b c*, with a receptacle R connected with the main flue from the absorbing-towers and chambers. This receptacle is also in communication

with a flue leading to the chimney, or other device for supporting the draught, and is divided by a partition having apertures fitted with valves or dampers D D, made of an alloy of lead and antimony. The operation of opening and closing D D to ensure uniformity of draught, is regulated automatically by the action of the suction itself in the following manner:—The dampers are connected to a lever B, mounted and turning on a centre or fulcrum *e*.

Fig. 117.

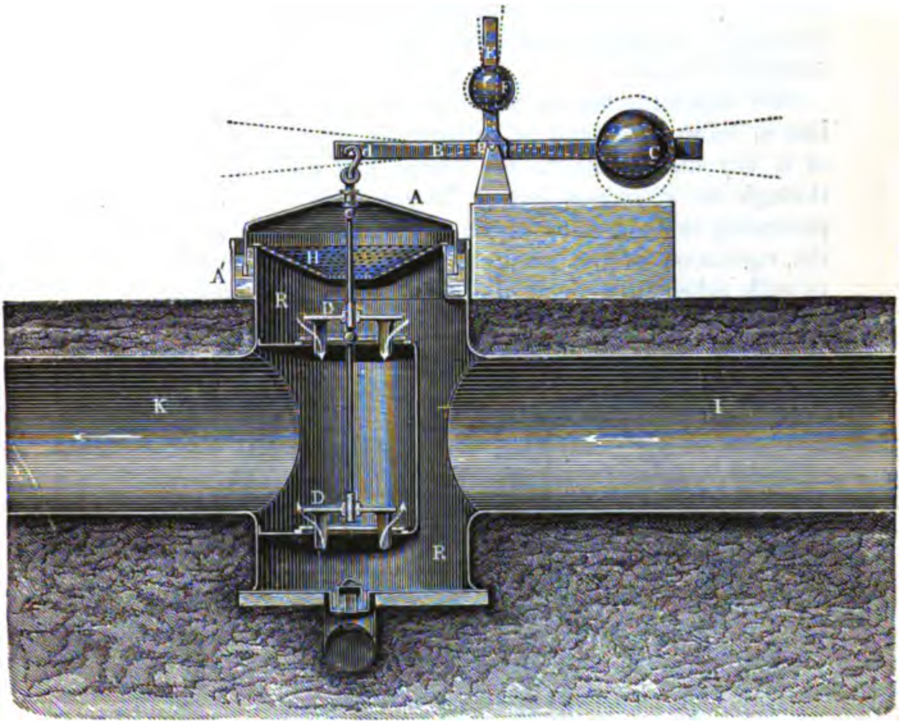



Suspended from one end of the lever is the vessel A, whilst the opposite end is loaded with a weight C, sufficient to preponderate to the required extent over the load of A. Assuming that the draught has an excess of "pull" over that which is adjusted and necessary for the proper working of the chambers, the dampers being open, the suction within the vessel A, when accelerated, will draw down that end of the lever and elevate the opposite or weighted end, and

so partially close the dampers. C is so calculated that the weighted end of the lever can only be elevated when the required draught is exceeded, and it will fall by gravitation as soon as the draught is unduly diminished. It follows that thus the desired uniform action is obtained.

The connexion between the dampers and the lever B is by means

Fig. 118.




of rods or links passing through water-sealed stuffing-boxes, G G[1]; and to avoid friction these rods are suspended from knife-edge centres $d\,d^1$. The other centres are constructed with knife-edges in like manner.

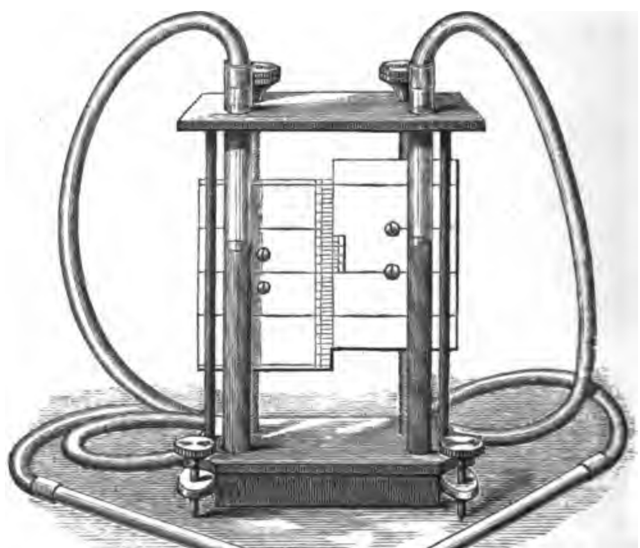
The vessel A becomes sensibly *lighter* when deeply immersed in the liquid, owing to the thickness of the sides, and would thereby constitute a source of disturbance to the proper action of the apparatus. To counteract this, the lever B is provided with a projecting

arm E, carrying an adjustable weight F, arranged in such a position that, as the arm partakes of the motion of the lever, the centre of gravity of the system will be moved in the direction and to the extent necessary to effect the required correction.

Fig. 118 is a simpler, and in some applications a convenient form of the apparatus, the action being of course identical with that described for the arrangement in fig. 117. Should the draught fluctuate very much, the diaphragm shown dotted at H (with an opening in its centre to communicate with the vessel A) can be interposed to prevent the movements of the regulator being too sudden and rapid.

This apparatus has no wearing surfaces, is practically frictionless in its working, and is balanced in all positions. By means of it any disturbance to the steady and uniform flow of gases through the chambers caused by irregular chimney-draught, is prevented, the admission of air to the burners is more uniform, the regulation of the proper quantity and relation of the gases to each other throughout the chambers is facilitated, and better

Fig. 119.



working and more economical results are obtained in the process with less supervision and attention than hitherto required to carry on successfully the manufacture of sulphuric acid.

To p. 332. *Fletcher's anemometer.*—The form shown in the text has been abandoned some time ago for a simpler one, shown in fig. 119. To this lenses have recently been added in front of the tubes containing the ether, which enable the readings to be made with extreme accuracy. These, however, are only needed when the speed to be measured is very low; in most cases the simple U-tube fitted with a vernier is quite sufficient.

To p. 341. *Fryer's anemometer*, described in the Inspectors' 'Report on the Alkali Acts' for 1877–78, p. 68, is stated to be the most delicate of all such instruments. Its principle is to measure the difference of pressure on each side of a watchglass-shaped copper plate, connected with a spiral spring. It will measure a pressure of $\frac{1}{3000}$ of an inch. Hitherto only one such instrument has been made, for Dr. R. A. Smith.

*Registering-apparatus for the Speed of Chimney-gases.*—Kuhlmann fils proposes to evolve coloured vapours at the foot of the chimney, and to observe the time which they take to reach the top (Année Industrielle, 1878, p. 67). This agrees in principle with Mr. Fletcher's experiments, where clouds of sulphuric acid vapour fulfilled the same purpose.

To p. 358. *Estimation of nitrogen compounds in the atmosphere of vitriol-chambers.*—Winkler (Industriegase, ii. p. 303) strongly urges frequent *quantitative* estimations, which, however, have hitherto been very rarely performed. He caused several such estimations to be made at the Mulden works, both by aspirating the chamber-gas, previously to its entering the Gay-Lussac towers, through acidulated permanganate till this was just discoloured, and by absorbing it in concentrated sulphuric acid for the purpose of titrating. A normally working chamber was found to contain 73 litres, a chamber short of nitre only 59 litres $N_2O_3$ in 100 cubic metres of chamber-gas—very small quantities indeed.

To p. 361. *Depth of acid in the chamber.*—M. Delplace decidedly denies, from his experience, that the process is improved by a great depth of acid at the bottom of the chamber. He was in a position to start a chamber (whose sides were burnt to the bottom) without any acid at all; the drops could be heard to splash upon the lead as they fell down from the top; yet both the yield of

acid and the consumption of nitre were as favourable as in any other case: the latter was below 1 part to 100 of the strongest vitriol.

To p. 362. *Rules for Working Acid-chambers* (according to communications from continental acid-works, made to the author by Dr. Robert Schlesinger).—Where one very long chamber is used (say 300 feet), the difference of temperature between the fore and the back part ought to be 20° C. The drips in the entrance-pipe ought to show 150° Tw., in the fore part of the chamber 134°, in the back part 76° Tw. The following short rules are employed for instructing the chamber-men, in most particulars the same as those given more explicitly in the text:—

1. *Temperature* (taken in the fore part of the chamber) *too low* shows want of nitre (pale chambers) or excess of draught (too much oxygen in the exit-gas).

2. *Colour too pale*: Want of draught in the burners (in this case there is enough draught behind); or want of draught altogether (then the oxygen in the exit-gas is too little); or want of nitre (chambers cold); or excess of steam (the acid drips drop too quickly).

*Too red*: excess of nitre.

3. *Hydrometer. Acid too weak*: excess of draught (chambers cold, too much oxygen in the exit-gas); or want of draught in the burners (no pressure behind); or want of draught altogether (too little oxygen); or want of nitre (chamber pale); or want of steam (acid drips drop too slowly); or excess of steam (drips drop too quickly).

*Acid too strong*: excess of nitre (chamber too yellow), or want of steam (drips drop too slowly).

To p. 363. *Control of the escape of acid vapour*.—Kuhlmann fils (Mémoires de la Société des Sciences, etc. de Lille, May 18, 1877) employs an apparatus somewhat similar to Mactear's; but in lieu of a gas-meter he has a reservoir of sheet-iron, serving at the same time as an aspirator.

The gases are deprived of their nitrogen- and sulphur-acids, and of their oxygen by five absorption-tubes charged with solutions of potassium permanganate, ammoniacal cuprous chloride, and soda; but how the several compounds are estimated at the same time is not explained. As he does not believe in the accuracy of anemometers in these cases, he measures the speed of the gases by

evolving vapours of nitrogen tetroxide from iron filings and nitric acid in a small furnace erected at the base of the chimney, and noticing the time which elapses before the red vapour appears at the mouth (compare also below, the Addendum to Vol. I. p. 573).

To p. 371. *Behaviour of the nitrogen oxides towards sulphuric acid.*—The following are the conclusions of a long research on the above subject which the author has published in Dingler's 'Journal,' vol. ccxxxiii. p. 63 (the conclusions are also published in the Ber. deutsch. chem. Ges. xii. p. 1058):—

1. Nitrogen tetroxide, under ordinary circumstances, cannot exist in contact with sulphuric acid, but at once splits up into nitrous acid, which, with a portion of the sulphuric acid, yields nitroso-sulphuric acid (chamber-crystals, or nitrosulphuric acid), and nitric acid (dissolving as such), thus:—

$$N_2O_4 + SO_2(OH)_2 = SO_2(OH)(ONO) + NO_3H.$$

2. Nitroso-sulphuric acid, on dissolving in an excess of sulphuric acid, forms a colourless liquid, but only up to a certain limit of saturation, which is so much the higher the more concentrated the vitriol. This limit for vitriol of sp. gr. 1·84 is not yet reached at 55·34 milligrammes $N_2O_3 = 185$ millig. $SO_2,OH,ONO$ in 1 cubic centim. of acid.

3. Beyond that limit at first a yellowish tint appears, of course with stronger acids only when more nitroso-sulphuric acid is present than with weaker acids. This took place with acid of sp. gr. 1·887 (made from pure vitriol of sp. gr. 1·84), containing in 1 cub. centim. 147 milligrammes $N_2O_3 = 372$ millig. $SO_2OH,ONO$, and also with acid of sp. gr. 1·706, containing in 1 cub. centim. only 56·7 millig. $N_2O_3 = 190$ millig. $SO_2OHNO_2$. Since these acids also are rendered colourless by prolonged boiling, the excess of nitroso-sulphuric acid seems to be rather loosely held; but the temperature of the water-bath is not sufficient to affect it.

4. The phenomenon observed by Winkler, a mixture of strong vitriol and nitrogen tetroxide showing an orange-colour even when cold, emitting red vapours, and exhibiting a tempestuous evolution of nitrogen tetroxide on being gently heated (which proves the existence of unchanged nitrogen tetroxide), can evidently take place only when the mixture contains *far* more $N_2O_4$ than the strongest mentioned above, or the strongest ever occurring in vitriol-works under any circumstances. Many experiments of

heating in the water-bath for a prolonged period demonstrate with certainty the absence of free $N_2O_4$ in all cases observed. Still less can the presence of nitrogen tetroxide be assumed in more dilute acids; it is therefore inadmissible to cite it as such in analyses.

5. All nitrous vitriols, *i. e.* solutions of nitroso-sulphuric acid in vitriol, whether they contain nitric acid at the same time or not, on being heated far below their boiling-point, assume a golden yellow or even darker yellow colour, but entirely lose it again on cooling. This change of colours may be repeated any number of times. It hardly indicates a loosening of the combination, since this proves to be very stable even at much higher temperatures; but it may rather be compared to the deeper colour which ferric chloride solutions assume on being heated.

6. The stability of nitroso-sulphuric acid in its solution in sulphuric acid is very great, even at the boiling-point, provided that the specific gravity is not below 1·70. It is true that on boiling it some nitrogen is always lost, and all the more the less concentrated the acid is; but if the boiling takes place so that the vapour cannot condense and flow back, there is some nitroso-sulphuric acid found in the residue, even from acid of sp. gr. 1·65. But if the vapour is condensed and the condensing liquid (which, in the case of vitriol of sp. gr. 1·80 or below, consists of very dilute acid or almost pure water) is allowed to flow back, a considerable loss is caused by denitration.

7. Down to a concentration of sp. gr. 1·65 the affinity of sulphuric acid for nitrous acid, *i. e.* the tendency to the formation of nitroso-sulphuric acid, is so great that any nitric acid present at the same time, whether added as such or formed by the decomposition of nitrogen tetroxide, is reduced with loss of oxygen, and employed to form nitroso-sulphuric acid. In the case of acid of sp. gr. 1·71 and upwards, this transformation takes place almost completely after a brief boiling, but at sp. gr. 1·65 only incompletely. This is a further argument against the existence of $N_2O_4$ in the solution.

8. Below sp. gr. 1·65 the nitroso-sulphuric acid possesses so little stability that, for instance, from acid of sp. gr. 1·60 some of it (but only a very small percentage) is expelled in the water-bath, and nearly all of it by boiling for a short time. In the case of acid of sp. gr. 1·5, it is evident that, even without heating, the nitrous acid added is partly decomposed into nitric acid and

nitric oxide; but after heating for an hour in the water-bath, considerable quantities of nitroso-sulphuric acid remain undecomposed, whilst another portion has been converted into sulphuric acid. In the case of still weaker acids, of course these phenomena occur even to a greater extent; but it is very probable that even very dilute sulphuric acid may contain, while cold, a little nitroso-sulphuric acid if reducing agents are absent.

9. Most of the nitric acid present along with nitroso-sulphuric acid in dilute acids (of sp. gr. 1·5 and under) remains behind in the liquid even after prolonged boiling. If, therefore, the nitrous vitriol of acid-works, in consequence of a faulty process, contains nitric along with nitrous acid, it cannot possibly be completely denitrated by hot water or steam, in which case a less strength than sp. gr. 1·5 is never reached; the denitration can be only effected by reducing-agents, such as sulphurous acid in the Glover tower or mercury in the nitrometer. In the latter it can be very clearly seen with how much more difficulty and slowness the denitration goes on in the presence of nitric acid.

10. The tendency to form nitroso-sulphuric acid is so strong that even if a large quantity of air (oxygen) is passed through sulphuric acid along with nitrous acid, no oxidation to $N_2O_4$ or $N_2O_5$ takes place, just as in the case of oxygen and NO.

11. Nitrous acid cannot be absorbed by caustic-soda solution without loss, because a portion of it is decomposed into nitric acid and nitric oxide.

12. The purple colour which is developed in nitrous vitriol by the action of reducing-agents, is caused by a solution of nitric oxide in such acids, and is possibly produced by a very unstable compound of nitrogen and oxygen, midway between NO and $N_2O_3$.

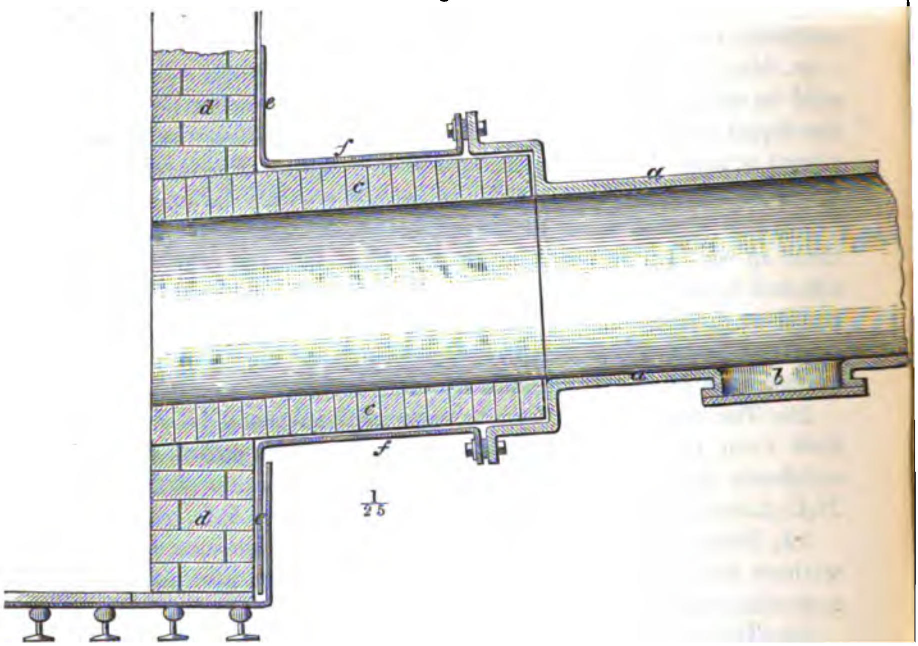
To p. 379. *Round absorbing-towers* have a square timber frame, to which, at every 6 feet of height, metal brackets are fixed; iron hoops, 3 inches broad, are suspended from these by means of hooks, closely girding the tower and supporting its lead shell.

To p. 434. *Construction of Glover towers.*—Delplace prefers the circular shape. The overlaps of the seams must in any case be placed outside. As packing he employed earthenware cylinders open at both ends, in irregular layers. These are light, and do not allow the flue-dust to lodge very easily.

To p. 435. *Introducing the burner-pipe into the Glover tower.*—

At most works the joint at this point is found leaky, owing to the difficulty of making a good joint between the hot iron and the lead. At Griesheim this difficulty has been entirely overcome by the construction shown in fig. 120. The burner-pipe *a a* (which

Fig. 120.




at *b* shows a cleaning-hole at the bottom) is enlarged at its end, so that it embraces one end of the dry-walled annular-shaped brick flue *c c*, whilst the other end is tightly held in the brick lining *d d* of the tower. The lead side of the latter (*e e*) is continued into a lead cylinder (*f f*) surrounding the free portion of the flue *c c*; its end is bent round in the shape of a flange, pressed against a flange of *a a* by means of an iron hoop and screw-bolts; and the joint is made tight by asbestos packing.

The bottom of the tower rests on railway-rails supported by brick pillars, and is thus quite accessible from below.

To p. 438. *Acid-distributing wheel* (*Barker's mill*).—This can be made entirely of glass, the spindle ending below in a glass globe about 4 inches in diameter, floating on acid in a glass or

lead trough. By this means the friction is perhaps rather increased; but there is no wear and tear as when the spindle ends below in a point, and no risk of jamming &c.

To p. 453. *The causes of the loss of nitre in the vitriol-manufacture*, and especially in the Glover tower, have been discussed at length in vol. xxxix. of the 'Chemical News' by Hurter, Davis, Jackson, Mactear, and the author (pp. 170, 193, 205, 215, 227, 232, 237). The following is a sketch of the more important results arrived at in that discussion:—Hurter assumes that, with a total consumption of 4 parts nitre to 100 sulphur, according to the results of seven works, 10·5 per cent. of the loss is accounted for by the nitre-gas present in the exit-gases, 10 per cent. by the incomplete denitration of the chamber-acid, and 5 per cent. by leakages of the chambers—altogether 25 per cent. "mechanical" losses of nitre, against 75 per cent. "chemical" losses by a too far-going reduction of the nitrogen oxides. None of this 75 per cent. loss occurs in the Gay-Lussac tower, in which no reduction of $N_2O_3$ to NO by $As_2O_3$ takes place, as asserted by Davis and others. He allows 20 per cent. for the chambers, leaving 55 per cent. of the loss of 4 parts of nitre, for which we can only look to the Glover tower.

The author replied that, notoriously and beyond fear of contradiction, at factories working with Glover towers there is not only no larger, but a smaller loss than with any other plan for denitration; the fear of a loss by the Glover tower has now vanished to such an extent that some manufacturers run even the fresh nitric acid through that tower. Even admitting, for the sake of argument, Hurter's calculation of the "mechanical" losses, his arbitrary assumption that of the "chemical losses" 20 per cent. are attributable to the chambers and 55 to the Glover tower cannot be granted; for at those factories where the denitration is effected in other ways the "mechanical" losses are no larger (as proved by statements of Kolb, Hasenbach, and Scheurer-Kestner on the nitre contained in their chamber-acid); these also require *at least* as much nitre as the factories employing a Glover tower; consequently the whole of the 75 per cent. loss must be ascribed to the chambers, and none of it to the Glover tower.

In his reply Hurter conceded distinctly that he did not intend to prove that an appreciable loss was actually experienced in the Glover tower, but merely that all fear of such a loss had not quite

vanished (*i. e.* on his part). He believes that he has elicited from the author the admission that the amount of nitre lost in a manner not yet clearly understood is 75 per cent., or more, of that used. He has no experience of any other method of denitration except by the Glover tower; and, for aught he can say to the contrary, it may be the very best means of denitration; but that does not imply that it is perfect. He believes that the conditions for reducing the nitrogen compounds below NO are present there to an equal if not a greater degree than in the chambers.

The author replied that after Hurter's own letter it was unnecessary to show any further that no proof of an appreciable loss of nitre in the Glover tower had been given, and he was content to leave that question where it stands. But he must repudiate having made the admission that 75 per cent. of the loss of nitre, or, speaking more definitely, a loss of 3 parts of nitre to 100 of sulphur, occurs "in a manner not yet clearly understood" or as "chemical losses." The "mechanical" losses must be much greater, and the "chemical" losses correspondingly smaller than they are assumed to be by Hurter; for many manufacturers, possessing better absorbing-plant, do not consume 4 parts, but only 2½ parts of nitre to 100 sulphur; it is credibly shown that these may be reduced to 1·6 part; and, admitting Hurter's assumption of 0·6 nitre to 100 sulphur as lost in the chamber-acid and by leakages, 1 part of nitre to 100 sulphur is the *maximum* of possible "chemical" loss. The real amount, however, cannot as yet be stated with any certainty.

The communications of Jackson and Mactear prove, indeed, that Hurter had greatly undervalued the "mechanical" losses. Jackson found, with a total consumption of 3·5 nitre to 100 sulphur, 40 to 50 per cent. of the loss in the exit-gases, whilst Hurter admits only 10 per cent. A great deal of nitre is also carried away in the chamber-acid; so that very little indeed is left for "chemical" losses. In the Gay-Lussac tower nitric oxide may be formed by the action of $SO_2$, which again accounts for a portion of the loss. Mactear, in a paper of some length, gives the results of continuous tests of large sets of chambers partly denitrating by Glover towers, partly by hot water. The losses in the exit-gas (apart from any NO) averaged 27·6 per cent. of the total nitre, or 1·3 to 100 sulphur. The loss in the chamber-acid amounted to 0–12·2 per cent. of the total at Glasgow, in a set without Glover tower, but 20·8 per cent.

at Newcastle (with Glover towers). The sets working with Glover towers consumed only 3·5, those denitrating with hot water 5·44 to 5·63 nitre to 100 sulphur. The decidedly greater "chemical" loss in the latter case seems to be caused by the irregular fitful evolution of the nitre-gas; this is also made probable by the fact that more nitre is consumed when it is decomposed in small pots in the kilns than when it is decomposed in large pots in the colder part of the flue.

By the above discussion it has been definitively proved:—1st, that the "mechanical" losses of nitre must be very much larger than assumed by Hurter from the results of seven works, evidently on the strength of insufficient analytical methods; thus, the "chemical" loss dwindles down to certainly less than 1 part of nitre to 100 sulphur (Jackson and Davis admit practically no loss in the chambers or towers by reduction of nitrogen compounds to $N_2O$ or N). 2nd, that the "chemical" loss in the whole set is less when denitrating is effected by a Glover tower than when it is done by hot water, probably owing to a more uniform action. Consequently even the *probability* of an appreciable loss in the Glover tower is absent; *proof* of it is not attempted by Hurter himself.

Cox (Chem. News, xxxix. p. 249) reports that, by doing away with the supply of liquid nitric acid, and introducing direct decomposition of nitre behind the kilns, he has saved $1\frac{1}{2}$ nitre to 100 pyrites, *i. e.* more than 3 nitre to 100 sulphur. This, however, must be owing to different causes, as some manufacturers, working with liquid nitric acid, consume hardly as much nitre altogether as Cox asserts he has gained by abolishing the use of liquid acid.

To p. 454. *Nitrous oxide in chamber-gas.*—Hitherto nitrous oxide has never been directly proved to be present, either in the chamber- or in the exit-gas—probably because no proper plan of testing for it was known. Winkler has now proposed one (Industriegase, ii. p. 427), viz. passing the gas over a palladium wire made red hot by a galvanic current; 2 vol. $N_2O$ thus split up into 2 vol. $N_2$ + 1 vol. O, which increase can be measured. But as probably the proportion of $N_2O$ will be too minute to admit of an exact measurement of that increase in the chamber-air itself, the author would propose the following plan:—Aspirate a large bulk of the gas through concentrated potash solution in order to fix the acids of sulphur and nitrogen; if NO should be present, remove this by shaking with permanganate solution, or by mixing a known

volume of oxygen with the gas before acting upon it with caustic potash. Then shake the gas with alcohol, which is a pretty good solvent for $N_2O$, expel the latter, and analyze it by Winkler's method *.

To p. 460. *Purification of sulphuric acid.*—According to the 'Journal of the Franklin Institute,' v. p. 65, at the works of Messrs. Merle & Co. (now Pechiney) iron, lead, and arsenic are removed by electrolysis.

Selmi (Gazz. chimica, x. p. 40) asserts that arsenic can be detected in acid which gives no reaction in Marsh's apparatus, by adding 300 grams water and some lead chloride to at least 1 kilog. of the acid, distilling, and testing the first portions of the distillate with sulphuretted hydrogen. Lead chloride can also be employed for completely removing the arsenic. The latter, according to Selmi, when present as arsenic acid, is not so fixed as is usually assumed; for about $\frac{1}{12}$ of it passes over on distillation.

To p. 490. *Construction of lead pans for boiling down sulphuric acid.*—Sometimes such pans, instead of being made of sheet lead burnt together, are *cast*, about $\frac{3}{4}$ inch thick. They are in that case exposed to the fire directly, without interposing iron plates. This plan cannot, however, be recommended. Such cast pans, being much thicker, are dearer than those made of sheet lead; and they are much more liable to have unsound places, which are very soon eaten through.

To p. 517. *Strength of concentrated oil of vitriol.*—Whilst only a few years ago the "strong" or "170° Twadd." oil of vitriol rarely exceeded 92 per cent. of $SO_4H_2$, more recently buyers of acid in Germany have required an acid of 95·5 to 96 per cent., which is about the strongest that can be practically made, either in platinum or glass. At 97 per cent. the loss of platinum is already too serious; and above that the acid does not increase in concentration, the distillate being as strong as the acid remaining behind. Stronger acids can only be made by adding fuming oil of vitriol. The statement that vitriol of upwards of 98 per cent. $SO_4H_2$ can be made directly in platinum is contradicted by very experienced practical men.

To p. 524. *Gridley's continuously acting glass retorts* are shown in detail in fig. 121. *a* is the head, connected with a draught-

* Since the above was written, the author has tried the plan proposed by Winkler, but found it not sufficiently accurate to be of practical use.

pipe common to all the retorts, by which the vapours are conveyed into a small leaden coke-tower and condensed by water. At *b* there is an opening in the shoulder of the retort; into this the funnel passes by which the acid enters the retort; *d* shows the level of the acid; *e* is the tubule attached to the retort, by which the acid leaves it; and *f f* show the glass connectors which convey the acid from one retort to another. The retorts are set in sand in shallow iron pots, *g*. Four beds of retorts, *i. e.* sixteen retorts, will produce, from 6 A.M. on Monday till 12 noon on Saturday, 600 carboys, equal to 46 tons; the labour required consists of two retort-men (day and night turns) and two labourers. The average consumption of coal is 28 lb. per carboy of 175 lb. (=16 per cent.). This process has for some years been in most successful operation in nearly all the vitriol-works in the United States, and is now being largely adopted by manufacturers in England (Mackenzie's 'Chemistry,' ii. p. 943).

Fig. 121.


The following further details have been kindly furnished to the author by Mr. H. C. D. France, of the firm of Messrs. Chance Brothers, Birmingham. The original patent was taken out on May 8th, 1871, by Mr. Henry Chance, as a communication from Gridley. The process is used in its entirety by Messrs. Chance Brothers, and also at several other English works, besides being almost universal in America. It has lately been very much improved at the above-mentioned works by using ordinary coal-gas as a heating agent, burnt in a Bunsen burner underneath each retort. This has largely increased the output and decreased the labour and breakage. The breakage during a period of two years has only cost 3*d.* per ton of acid rectified; and the labour has been 1*s.* 10*d.*; but this item could easily be lessened, as the same men could look after plant turning out twice as much. The gas consumed (made at the works themselves), with all leakages and defects, has been 3500 cubic feet per ton of acid of sp. gr. 1·845. By further improvements in the burners and the setting of the glasses, now in

progress, Messrs. Chance expect to materially reduce the quantity of gas consumed.

To p. 535. *Concentration of sulphuric acid on Prentice's system.*—Further statements on this point, concerning the apparatus working at Griesheim, have been made in the 'Chemische Industrie,' 1879, p. 309. The output has risen from 6 tons to 10 tons of strong vitriol per day. As the direct heat applied to the boiler containing the strongest acid damaged the platinum too much, the platinum pan containing the weakest is now put over the fire, which afterwards passes first under the stronger pan, then under the boiler where the final concentration takes place, at last under the six lead pans which bring the chamber-acid up to about 140° Tw. The platinum is now quite safe; but a saving in coal has not been effected. The leaden cooler for the distilling acid has been replaced with great advantage by a platinum pipe 5 feet long by 2 inches wide [similar to Delplace's, see below]. The vitriol shows on running into the first pan (measured at 15° C.) 134° Tw., into the second pan 155°, into the boiler 165° Tw. The distillate shows from the first pan 0°, from the second 15° to 18°, from the boiler 85° to 90° Tw. The cost of plant for different systems is shown in the following table:—

| | Concentrates vitriol per day. | Cost. | Cost per ton of vitriol. | Concentrates for equal cost of plant. |
|---|---|---|---|---|
| | tons. | £ | £ | |
| Old platinum still | 7·5 | 3760 | 500 | 38 |
| System of Desmoutis and Co. | 4·8 | 1200 | 250 | 76 |
| " of Faure and Kessler | 5·0 | 1200 | 240 | 79 |
| " of Prentice | 10·0 | 1880 | 190 | 100 |

The favourable proportion exhibited by Prentice's plan is principally owing to the corrugated bottom of the pans, which increases the heating-surface in the proportion of 1·57 to 1. The thin stratum of acid is a feature common to all more recent plans.

To p. 536. *Platinum retorts, system "Delplace."*—According to information received from M. Delplace, he has replaced the form of still represented in the text by another, represented in figs. 122 to 124. In these A A means the first platinum still, which is fed with acid of 144° Tw., and the distillate from the still B B. The latter, also of platinum, carries on the concentration up to a percentage of 79 or 80 per cent. $SO_3$. C C are heads and arms,

with outlet at D for the strong distillate; the weaker not condensed vapour goes away at E. F is a bottle-shaped cooler for receiving the concentrated acid from the stills. G is a piece attached to the first still for receiving the acid from the lead pans and the distillate from B B. H is a tube for receiving the condensed distillate and carrying it back to A A. In this apparatus the vitriol may be brought to 79 or 80 per cent. $SO_3$, which hitherto has never been attained with continuously working apparatus, least of all with that of Faure and Kessler. If this stronger acid, indispensable in the manufacture of dynamite &c., is made, the distillate

Fig. 122.

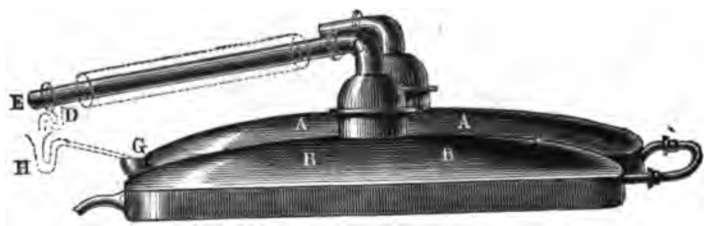
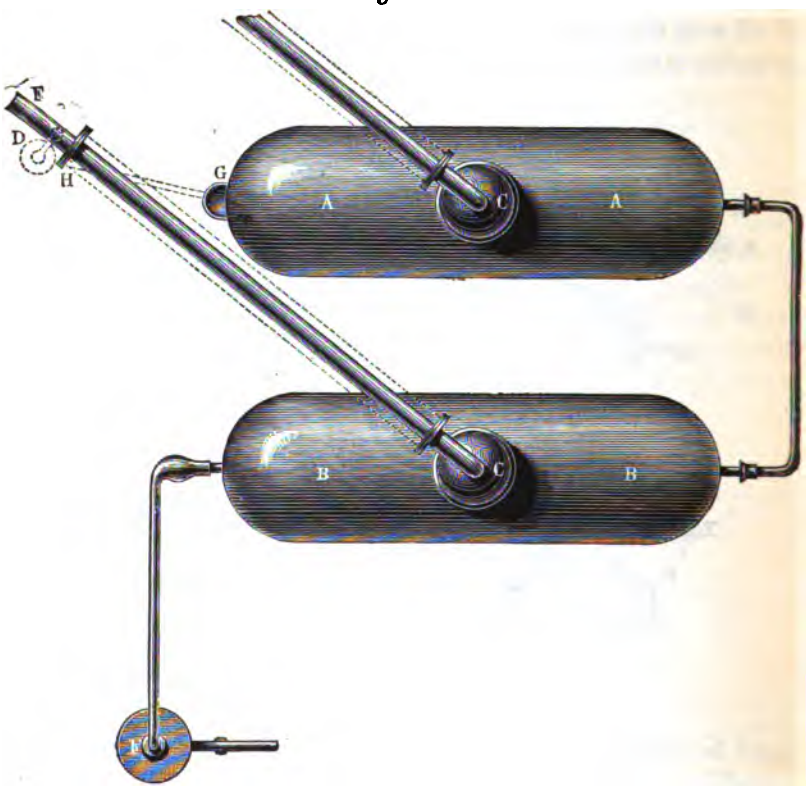



Fig. 123.


must be allowed to get up to 150° or 155° Tw., and is always conveyed back to the first still. For making the ordinary stronger vitriol, so-called "170° Tw.," which really only contains 73 to 76 per cent. $SO_3$, the distillate should only show 7° to 23° Tw., according to the speed of work, the feed-acid being 144° Tw. strong. The following advantage is claimed for the rectangular shape of still—that in working for the most highly concentrated vitriol, the ferric sulphate cannot collect in the opening of the discharging pipe, which generally happens with the ordinary apparatus; the distillate

is also said to be weaker, the output larger, in proportion to the evaporating surface, and the consumption of coal smaller than with the round shape. Instead of lead coolers, the distillate is condensed by a platinum tube 2¼ inches wide, which is cooled by water for a length of 5 feet; along with the head it weighs no more than the former large head and arm for connexion with a

Fig. 124.




lead cooler, without being liable to the frequent need of repairs of the latter; it also permits condensing vitriol of any strength, free from lead. Consequently the concentration may be carried to any required extent, whilst with lead condensers, and still more with lead-covered platinum dishes, the great wear and tear of the lead does not permit this.

For making the very strongest vitriol by a continuous process

(which previously was quite impossible), two long stills are preferable to one, the distillate from the second still running back into the first quite hot, without contact with lead; only the first weak distillate escapes. The stills are placed straight over the fire-grate, so that the heat of the fuel is well utilized. The following table gives the strengths of the distillate for concentration to different strengths, assuming the apparatus to be fed with acid of 140° to 144° Tw. :—

| Strength of Concentrated Acid. Per cent. $SO_3$. | Strength of Distillate. Degr. Tw. |
|---|---|
| 75 | 15–18 |
| 76 | 23–32 |
| 77 | 51–63 |
| 77½–78 | 88–103 |

When a system of two stills is employed :—

| Strength of Concentrated Acid. Per cent. $SO_3$. | First Distillate. Degr. Tw. | Second Distillate. Degr. Tw. | Both mixed Degr. Tw. |
|---|---|---|---|
| 75 | 0–3 | 15 | 9 |
| 76 | 3–7 | 23–31 | 15–18 |
| 78 | 23–28 | 75–88 | 52–64 |
| 79–80 | 41–75 | 144–150 | |

The second distillate runs back into the first still.

Amount of work of an apparatus for different strengths of concentrated acid per 24 hours :—

| | | | |
|---|---|---|---|
| 75 per cent. $SO_3$ | . . . . . . | 12 tons. |
| 76 „ „ | . . . . . . | 10 „ |
| 77 to 78 „ „ | . . . . . . | 8 „ |
| 79 to 80 „ „ | . . . . . . | 5 „ |

The last, strongest vitriol has hardly been in the market hitherto. It is easily seen from the above that concentration up to that point is much more costly than that of less strong acid; but for some purposes, especially for manufacturing nitroglycerine, the very strongest vitriol is in great request. The value of such acids cannot possibly be estimated by the hydrometer, both because this is no longer accurate at that point (vide Vol. I. p. 28), and because

the iron and lead always present in the acid influence its specific gravity. Recourse must therefore be had to alkalimetrical tests.

The cooling of the concentrated acid is done by an upright platinum cylinder, standing in water. The acid enters at the top, and leaves it at the bottom; the water enters the outer vessel at the bottom, and leaves it near the top.

The apparatus is supplied by Messrs. Johnson, Matthey, and Co. by weight, at market prices for platinum. The weight of one boiler is about 50 lb.; head, condenser, and acid-cooler together 17½ lb. With this 5 tons of vitriol of 93 to 94 per cent monohydrate, or 6 tons of 92 per cent. monohydrate (the common "170° Tw.") are made. A two-boiler apparatus, weighing about 110 lb. with all appurtenances, furnishes 10 tons of vitriol at 93 to 94 per cent., or 12 tons at 92 per cent. in 24 hours. M. Delplace (St. Croix 10, Namur) undertakes the erection and starting of the apparatus.

To p. 551. *Apparatus of Faure and Kessler.*—In a pamphlet, published in 1878, they describe their newest improvements, said to be very important. In place of the double lead ring cooled with water which makes the hydraulic lute for the leaden hood of the older apparatus, and which is very liable to get out of repair, a platinum gutter is formed round the margin of the dish itself, as shown in the section, fig. 125. J J is this gutter, *c c* a cast-iron ring for supporting the dish, *f f* another cast-iron lead-covered ring for supporting the gutter J J; between the two is the discharge-tube *t*. The distilling acid runs out of the gutter through the tube *d*.

Fig. 125.


To p. 555. ***An explosion on cleaning out a platinum still*** has been reported by Kuhlmann fils. It occurred by running water upon some acid left in the still (the two strata evidently remaining

separate), and starting the fire. At a certain point the two strata must have become suddenly mixed; and the explosion occurred through a violent evolution of vapour.

*Loss of platinum in concentrating vitriol.*—Messrs. Schnorf, at Uetikon, state the loss of platinum in their Faure-and-Kessler apparatus at 0·75 gram platinum per ton of ordinary so-called 170° vitriol; for the strongest acid (say really $=168°$ Tw.) the loss is as much as 10 grams per ton.

To p. 556. *Concentration of sulphuric acid in cast-iron pans* is once more proposed by Hartmann (patent 2839, 1879). The acid is to be saturated with iron salts, which are again separated on concentration, and are intended to protect the iron of the pan itself. (It is very doubtful whether this plan will answer.)

A similar object is aimed at by Nobel in a totally different way (Germ. patent 10149, 1880). Since cast-iron is not acted upon by the *vapour* of sulphuric acid, the concentrating-apparatus is made in the shape of a column consisting of cast-iron pipes, in which porcelain dishes are placed on ledges. Each dish has an opening, through which a glass rod reaches into the next lower dish; this is intended to prevent the acid from splashing about in its downflow from dish to dish. When all the dishes are filled, the column is heated by flues surrounding it on the outside. The acid vapour, as well as the concentrated vitriol, is taken away at the bottom. Even nitrous vitriol is said to be used in such towers.

To p. 560. *Packages for sulphuric acid.*—Leaden cylinders cannot very well be employed, because the lead is rendered brittle by the shaking during the transit, and is soon cracked. For acid of 144° Tw., and upwards, either cast-iron or wrought-iron vessels are generally used in Germany; but the vitriol should not be too nitrous. Chamber-acid cannot be carried in this way, especially because it always contains a certain quantity of nitrous acid. At Griesheim the difficulty is met by surrounding a lead cylinder with a sheet-iron jacket, perforated by many 1-inch holes, and tinned; the lead, tin, and iron can then be united intimately by applying heat. Even then the lead is liable to crack, unless the cylinder is supported in a wooden trough lined with cow's hair, and resting on good springs.

According to Kuhlmann fils (Société industrielle du Nord de France, 1878), wooden tubs lined with lead do not stand the shaking of transit on cart-roads; but wrought-iron vessels stand

Fig. 126.

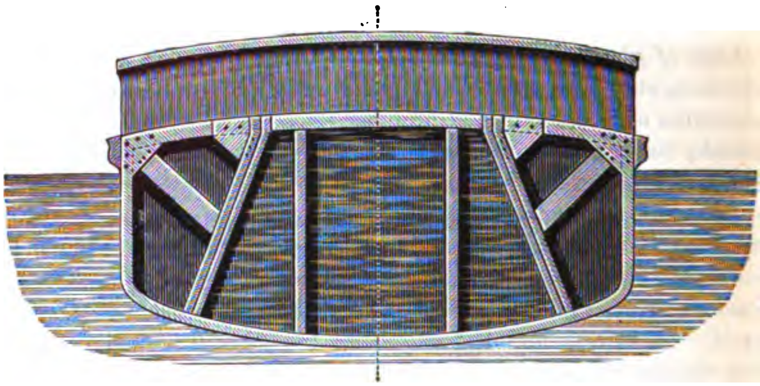


Fig. 127.

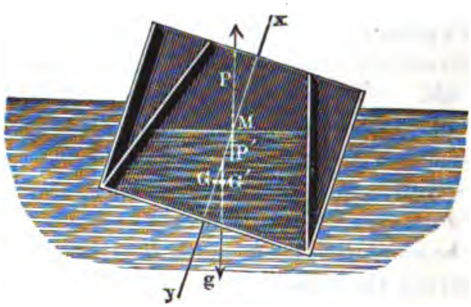
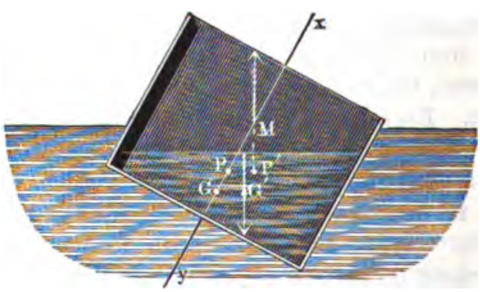



Fig. 128.



very well, if the air is excluded, for acids ranging from 140° to 170° Tw. Such vessels having a capacity of 6 or 8 tons are employed for railway-trucks, and of 2½ tons for cart-traffic. Canal-boats for the same purpose are subject to dangerous shiftings of the centre of gravity by the oscillations of the acid; but this is entirely prevented by making longitudinal partitions, leaving an air-space widening out at the top, as shown in fig. 126. It is apparent from fig. 127 that in such a case the shifting of the centre of gravity is very slight as compared with the ordinary system (shown in fig. 128).

Holden (patent No. 3805, 1877) proposes to construct acid-tanks from wood which has previously been warmed and soaked with paraffin. The edges are to be made tight by a solution of gutta percha in naphtha.

To p. 573. *Losses of sulphur and nitre in vitriol-making.*—According to the Inspectors' Report for 1877–78, p. 69, the chamber-escape was, in grains per cubic foot:—

| | Acidity as $SO_3$. | Nitrogen oxides as $N_2O_3$. | Total acidity of chimneys. |
|---|---|---|---|
| No. 1 district (South Lancashire, etc.) | 1·64 | 0·185 | 0·73 |
| „ 2 „ (Midland Counties, etc.) | 4·07 | ...... | ...... |
| „ 3 „ (Newcastle) ............... | 1·83 | 0·35 | 0·96 |
| „ 4 „ (Scotland and Ireland). | 2·77 | 0·237 | 0·983 |

In order to obtain a certain uniformity, a Committee appointed by the alkali-makers adopted the following mode of testing for and estimating the amount of acid in gases:—

### *Sulphur- and Nitrogen-acid Escapes.*

A continuous test over 24 hours to be taken of the gases escaping from the exit-pipes of the Gay-Lussac towers. The number of cubic feet of chamber-space per pound of sulphur burnt and passing into chambers in 24 hours to be recorded (excluding towers, but including tunnels). The amount of sulphur burnt per day, upon which these calculations are based, must be taken on the weekly average; each firm to state the distance of the testing-hole from the point at which the gases leave the Gay-Lussac towers.

*Absorption-apparatus to consist of* four bottles or tubes, containing not less than 100 cub. centim. of absorbing-liquid, with a depth of at least 3 inches in each bottle. The aperture of inlet-tubes

not to exceed $\frac{1}{50}$ inch in diameter; a standard wire for measuring this will be supplied.

*Absorbing-liquids.*—In the first three bottles, the solution to be 100 cub. centim. of normal caustic soda (31 grams per litre), and in the fourth bottle 100 cub. centim. distilled water. The caustic soda used to be proved free from nitrogen acids.

*Speed of aspiration and quantity of gases.*—As nearly as possible 24 cubic feet in 24 hours at a constant rate. Any aspirator securing a constant rate of aspiration may be used.

*Temperature and Barometrical Pressure* to be recorded, and corrections made to 30 in. bar. and 60° F. Where the "Mactear" meters are used, a maximum- and minimum-thermometer must be enclosed in the same room in which the meter is placed. The average reading of these two thermometers must be considered the mean temperature for the 24 hours. The average reading of the barometer at beginning and end of the 24 hours must be taken as the mean barometric pressure for that period. If the reading of the meter was C cubic feet, the average temperature T degrees Fahrenheit, and the mean barometric pressure B inches, the reduced volume of gases at 60° and 30 in. will be

$$V = \frac{C \times B \times 519}{30 \times (459 + T)}.$$

Where an ordinary aspirator is used (which must, however, hold 24 cubic feet and be so arranged that the water flows out at a constant rate), a thermometer must be fixed to show the temperature, and a small mercurial gauge to show the pressure inside the aspirator. The barometric reading at the time of measuring the gas must be taken, and the difference of pressure indicated by the gauge must be deducted from the barometric reading, before the correction indicated by the above formula is calculated.

*Mode of testing.*—The washings of the gas must be tested for total amount of acids, and for the amount of nitrogen acids they contain. The difference between the two tests is to be calculated as sulphur-acids. The results are to be stated as follows:—1st, total acidity in grains of sodium carbonate neutralized per cubic foot of gas; 2nd, the acids to be stated as grains of sulphur per cubic foot, and as grains of nitrogen per cubic foot.

The analysis must be carried out as follows:—The contents of the four bottles are united, taking care not to unnecessarily aug-

ment the bulk of the liquid. They are divided into three equal parts. The 1st part is simply titrated with normal sulphuric acid (49 grams $H_2SO_4$ per litre). Suppose $x$ cubic centims. of acid were necessary to complete neutralization. The 2nd part of the liquid is gradually poured into a warm acid solution of potassium permanganate, strongly acidified with pure sulphuric acid. A small excess of permanganate must be present, and afterwards reduced by the addition of a few drops of sulphurous acid solution, until only a faint red tint is visible. This faint red tint must be observed, to make sure that all the nitrogen is present in the form of $HNO_3$, and that no excess of sulphurous acid has been added. The solution, containing all the nitrogen in the form of nitric acid, is transferred into a flask containing a solution of ferrous sulphate equivalent to 2·8 grams of metallic iron. 100 cubic centims. of iron solution containing 28 grams of iron per litre will be found very convenient. An acid solution of ferrous sulphate can be kept for some time without appreciable change; and any change can easily be ascertained from time to time [this should be done once a day.—G. L.]. The flask containing this iron solution is closed by a cork with two perforations. A current of carbonic acid passes through the flask, and thence issues through a tube ending beneath the surface of some water, to prevent entrance of air. Before the solution about to be tested is introduced into the flask, the air is expelled by this current of carbonic acid, which must be evolved in an apparatus permitting a constant evolution for some time, without recourse to intermittent feeding with acid through a funnel-tube, an operation which would be sure to introduce air into the apparatus. After the nitrate solution is introduced into the acid iron-solution (the mixture should contain at least 20 per cent. of free sulphuric acid) and all air is expelled, the contents of the flask are heated to boiling, and kept boiling until the dark colour which appears when any appreciable amount of nitric acid is present has changed to a clear sherry-colour. The reaction is now complete; and the amount of ferrous sulphate left unoxidized is ascertained by titration with normal potassic permanganate solution, or a bichromate solution of such strength that 100 cubic cent. =2·8 grams metallic iron. Suppose $y$ cub. centims. of this standard solution have been used.

The 3rd portion of the liquid is reserved for the purpose of repetition in case of accident or doubt.

If $x$ cub. centims. normal acid and $y$ cub. centims. normal permanganate have been used, and V cub. feet of gas at 60° F. and 30 inches barometric pressure have been drawn, the following calculation will give grains of sodic carbonate, sulphur, and nitrogen per cubic foot of gas:—

$$\text{Total acidity} = \frac{2{\cdot}454 \times (100 - x)}{V} \text{ grains } Na_2CO_3;$$

$$\text{Sulphur} = \frac{0{\cdot}12346 \times (500 - 6x + y)}{V} \text{ grains S};$$

$$\text{Nitrogen} = \frac{0{\cdot}10803(100 - y)}{V} \text{ grains N}.$$

(1 gram = 15·43235 grains.)

To these instructions we have but very little to add. It is perfectly right not to attempt to estimate sulphurous and sulphuric acid separately in an alkaline absorbent, which would give quite erroneous results. Whether the alkalimetrical test will be accurate in the presence of sulphites and nitrites is doubtful. No account is taken of nitric oxide, NO, which notoriously escapes when the chamber-process is at fault. This might be provided for by adding another absorbing-bottle charged with a mixture of concentrated sulphuric acid and a little nitric acid of known strength. The NO would at once reduce the nitric acid ($4NO + N_2O_5 = 3N_2O_3$); and nitrososulphuric acid would be formed, which might be estimated in a few minutes by the aid of the "nitrometer" (Vol. I. p. 66, and Vol. III. p. 338). It seems easier to pass the NO through potassium permanganate and retitrate this; but the permanganate acts too slowly on nitric oxide diluted with an enormous bulk of other gases. Or air may be mixed with the gas after passing it through the alkaline absorbent, so that higher oxides of nitrogen will be formed and absorbed in pure sulphuric acid. Mr. Davis has proposed hydrogen peroxide, which reagent is not always easily procurable, at least of reliable strength. This method is described in detail in 'Chem. News,' xli. p. 188. Since even a strongly acidified solution of ferrous sulphate changes pretty quickly, it must be standardized every day with the potassium permanganate (what the instructions call "normal" perman-

ganate, is the same solution as that generally prescribed in this treatise, called "seminormal" because it yields 0·004 gram oxygen per cubic centim.). It is out of the question to modify the iron-solution constantly so that it shall remain equivalent to 2·8 Fe as a ferrous sulphate; but this is unnecessary if in the last of the above three formulæ the number of cub. centims. of permanganate required for 100 cub. centims. iron solution (call it $z$) be put in the place of 100, and if in the second formula the figure 500 be replaced by $600-z$.

W. E. Strype has constructed a very ingenious *aspirator and absorbing-apparatus*, not liable to get out of order. It is described in the 'Transactions of the Newcastle-on-Tyne Chemical Society,' vol. iv. p. 357 *et seq.*

To p. 577. *Calculation of Sulphuric Acid at a Swiss Works.*—

| | fr. | c. |
|---|---|---|
| 2 tons 10 cwt. of pyrites at 2 frs. 25 c. per cwt. | 112 | 50 |
| 3·4 cwt. of nitrate at 22 frs. 30 c. per cwt....... | 75 | 82 |
| 4 men at 3 frs. 50 c................................ | 14 | 0 |
| Sundries ........................................ | 3 | 80 |
| General expenses (and coals) ..................... | 38 | 0 |
| Small stores......................................... | 4 | 0 |
| Repairs.............................................. | 14 | 0 |
| 105 cwt. of vitriol at 50° Bé (=106° Tw.) ...... | 262 | 12 |
| 1 " " " " | 2 | 50 |

F. Curtius (the owner of a large vitriol-works at Duisburg, on the Rhine) discusses at length the cost of sulphuric-acid-making, in order to complete the statements of Vol. I. of this Treatise (Chemische Industrie, 1879, p. 187). His own statements are of great interest, as they refer to old-established works, whose produce of vitriol was almost entirely sold as such, whilst the author's figures refer to works where all general expenses were charged to alkali. The following costs all refer to vitriol concentrated to 144° Tw. by steam-heat (comp. Vol. I. p. 503), exclusive of packages and transit. We only give the maxima, minima, and averages of the 14 years over which the figures range, viz. 1865 to 1878, in shillings per ton:—

| | Minimum. | Maximum. | Average. |
|---|---|---|---|
| (1) Wages | 5·36 | 8·48 | 6·55 |
| (2) General expenses (Management, Insurance, Rates, Taxes, Lighting, Cartage) | 3·40 | 4·73 | 4·23 |
| (3) Office-expenses (without commissions, etc.) | 1·98 | 2·77 | 2·32 |
| (4) Repairs | 3·31 | 9·31 | 5·93 |
| (5) Amortization of plant (5 per cent. on old, 10 per cent. on new plant) | 2·24 | 3·72 | 2·83 |
| (6) Interest on capital | 3·11 | 4·25 | 3·56 |
| Total | 21·58 | 33·10 | 25·42 |
| Extra expenses for new plant | ...... | 6·63 | 1·61 |
| Annual working-days | 304·4 | 352·4 | 329·4 |

If the acid had to be sent out in glass carboys, which were returned by the buyer, this caused an expense of 4*s*. to 6*s*. per ton; but sending it out in copper or lead-vessels only cost from 0·6 to 1*s*. per ton for repairs etc., of course exclusive of carriage.

To p. 579. *Treatment of burnt pyrites for iron.*—Faur (Germ. patent, No. 8730, May 22, 1879) proposes to treat the crushed pyrites cinders with a solution of alkaline permanganate, by which sodium-sulphate and $MnO_2$ are formed. The first is washed out; and the residue forms a manganiferous iron-ore.

To p. 587. *Extraction of copper from burnt pyrites.*—P. Spence (comp. Inspectors' Report, 1877–78, p. 48) burns the pyrites (finely ground) in a furnace similar to his old one (Vol. I. p. 188), but with the aid of mechanical stirrers that plough up the ore into ridges, making a change of surface every 2½ minutes. He asserts that in this way he burns three tons of ore in a furnace in a day, and renders all the copper soluble to 0·24 per cent.; thus he is able to wash out the copper-salt and avoid the subsequent roasting with common salt. As much as 4·6 per cent. of sulphuric acid is left in the ore, rendering the copper soluble.

To p. 613. *Treatment of burnt Pyrites containing Lead.*—The lead remains behind as sulphate, mixed with the purple ore and injuring its quality as an iron-ore. Schaffner (private communication) removes and utilizes the lead in the following simple and cheap manner. After roasting the ore with common salt as usual and washing out all soluble chlorides and sulphates, the residue is drenched with chloride-of-calcium liquor (from the Weldon chlorine process) of 9–12° Tw., heated to about 40° C., and acidulated with hydrochloric acid. By mutual decomposition gypsum and lead chloride are at once formed, which remain *dissolved* in the

acid liquor. This is run off and brought into contact with metallic iron, which precipitates the lead in the metallic state. After washing, the purple ore is quite free from lead sulphate. At the same time the $CaCl_2$ dissolves the last traces of copper and silver, present as $Cu_2Cl_2$ and $AgCl$; these are precipitated along with the lead. It should be noticed that sulphuretted hydrogen fails to indicate the lead in a solution of $PbCl_2$ in $CaCl_2$ acidulated with $HCl$.

To p. 640. *Manufacture of sulphuric anhydride by Wolters's process.*—An additional German patent (No. 6091, Oct. 13, 1878) contains a simplification which the author in his laboratory-experiments had employed as a matter of course. Instead of treating the residue from distillation with water and separating the salts by crystallization, the dry double salt ($Na-SO_4-Mg-SO_4-Na$) is ground and treated directly with sulphuric acid (1 equivalent to 2 of salt, as otherwise half of the acid passes over in the hydrated state).

To p. 646. *Manufacture of sulphuric anhydride by catalytic action.*—The author is informed by Dr. Messel that the process patented by himself and Mr. Squire was discovered quite independently of Winkler, and without any knowledge of his process.

To p. 648. *Manufacture of sulphuric anhydride.*—According to communications received direct from Dr. Majert (formerly the largest continental manufacturer of fuming vitriol and anhydride), the only process for this purpose which has stood the test of prolonged practical trials is that of Winkler himself, with properly constructed apparatus. That employed by Majert at the Schlebusch works, near Cologne, was arranged as follows:—The decomposition of sulphuric acid into $SO_2$, O, and $H_2O$ was effected in upright retorts made of a mixture of 3 parts burnt fireclay broken to the size of a pea, and 1 part best Belgian fire-clay, and glazed with a mass which at the highest temperature of the process becomes pasty but not liquid, so that any cracks occurring in the retort fill themselves up with the glaze. The retorts are perpendicular, entirely surrounded by the fire, and closed at top and bottom by hydraulic joints. The top joint serves for introducing the pipe conveying the acid to be decomposed, the bottom joint for making the sides of the retort tight in the fixed bottom, which is perforated by the pipe which carries off the gases. Both the "hydraulic" joints, which are entirely surrounded by the fire, are

luted with melted glass. Within the first retort there is a cylinder, into which the vitriol flows from a small platinum tube, so as not to touch the sides of the retort at all. It is thus evaporated within the inner cylinder, and is partly decomposed already there, partly in the annular space between the cylinder and the retort, and completely in the second retort. The vapour and gases are conveyed from the first to the second retort by a twice bent tube, which passes through the bottoms of both retorts, and whose horizontal part is surrounded by the flame of the fireplace. The gases pass away from the top of the second retort into a condenser for liquefying most of the water, then into a drying-tower, and at last into the apparatus for uniting $SO_2$ and O, consisting of cast-iron retorts filled with wire-gauze shelves, upon which the platinized asbestos is spread.

An English patent of Messel's (Jan. 15, 1878) prescribes burning sulphur by means of oxygen, obtained by the electrolysis of acidulated water with the help of dynamo-electrical machines. The sulphurous acid formed, mixed with the excess of oxygen required for forming $SO_3$, is conveyed into a gas-holder, from which the gases are carried at a high temperature over spongy platinum, platinized asbestos, oxide of chromium, iron, or copper. The anhydride formed is condensed by itself or absorbed in sulphuric acid. By employing two gas-holders the process is made continuous. The electrolytical hydrogen formed at the same time is employed for heating, or it is carburetted and employed for lighting.

According to a German patent of Squire's (No. 4285, March 3, 1878), strong vitriol is introduced into a red-hot tower packed with hollow bricks and previously filled with dry steam. The vitriol is in the form of a mist, produced by a compressed gaseous mixture of sulphurous acid and oxygen. The products of decomposition are conveyed in a horizontal closed channel through a lead pan filled with dilute sulphuric acid, where the water is condensed by cooling, whilst the heat of the gases concentrates the sulphuric acid contained in the pan and frees it from sulphurous acid. A further condensation takes place in cooling-pipes; and ultimately the gases are dried in a coke-tower by means of strong sulphuric acid, which is again concentrated and freed from $SO_2$ in the lead pan just mentioned. The dry mixture of $SO_2$ and O is combined into $SO_3$ in a specially heated apparatus of cast iron out-

side and brickwork inside, fitted with a pyrometer, where it is brought into contact with platinized asbestos, being forced to travel a circuitous path between courses of bricks. The vapour of anhydride is absorbed by strongest vitriol in a cast-iron tower, fitted with dishes of a peculiar shape, placed one on the top of another. (The specification gives further details and diagrams of the apparatus.)

A German patent of Cl. Winkler's (No. 4566, Sept. 21, 1878) describes the preparation of *extremely active catalytical substances* from precious metals or metallic oxides in the finest state of division, with which an indifferent porous matter is impregnated almost in the same way as a textile fabric is dyed in the beck. The best catalytical substance is platinum, also iridium or palladium, less so the oxides of iron, chromium, manganese, cobalt, and copper. As an indifferent menstruum almost any loose porous body may be used, preferably asbestos, but also glass wool, pumice, infusorial earth (Kieselguhr), clay, and, where a very high temperature is not required, even cellulose, cotton wool, gun-cotton, sponges, etc.

In order to charge asbestos with finely divided platinum, it is thoroughly soaked with a solution of platinum chloride made alkaline by soda and mixed with sufficient sodium formiate to reduce the platinum. The well-wrought pasty mixture is dried in a water-bath; thus the platinum is separated as "platinum-black," and is firmly precipitated upon the fibre. The salts are removed by washing, without washing off the platinum. The quantity of the latter precipitated depends upon the strength of the solution of platinum chlorides; with asbestos or cotton-wool a percentage of 80 platinum may be attained. Metallic oxides exhibit catalytical action only at higher temperatures, and, accordingly, must be precipitated upon fire-proof substances. Thus asbestos or pumice may be thoroughly impregnated with chromium oxide by soaking in mercurous nitrate, then in ammonium chromate, drying each time, and ultimately gently igniting. Cupric oxide is precipitated firmly by soaking in an ammoniacal solution of cupric carbonate and gently igniting. Asbestos may also be soaked with solutions of manganous or cobaltous chloride, etc., dried, put into a heated solution of bleaching-powder or of another precipitant, dried again, washed, and ignited. The contact-substances prepared in this wise, owing to their homogeneous condition and

their very large surface, cause, either at the ordinary or at a higher temperature, the combination of certain gases, such as that of $SO_2$ and O into $SO_3$, the conversion of the $CS_2$ in coal-gas into $H_2S$, the oxidation of the vapour of alcohol, etc. They may be employed for all reactions based upon the phenomena of so-called "catalytic action."

*Utilization of the sulphuric anhydride contained in pyrites kiln-gases.*—Majert and Messel (Engl. pat. No. 1201, March 26, 1878) pass the kiln-gas through concentrated vitriol, which dissolves the sulphuric anhydride, and is thus converted into real monohydrate, $SO_4H_2$ (but at the same time dissolves much $SO_2$!).

To p. 649. *Manufacture of sulphuric acid without lead chambers.*—Houzé proposes (Monit. Industr. v. 7, p. 65) to bring sulphurous acid, air, and steam into contact in stoneware vessels at a tempeperature a little below a read heat. Similar vessels are said to permit distilling the acid by means of heated air or superheated steam without any bumping.

## ADDENDA TO VOL. II.

To p. 12. *Analysis of Sulphate.*—Grossmann (Chem. News, xli. p. 114) estimates the sulphate directly by adding barium hydrate, filtering from the $BaSO_4$, precipitating the excess of barium hydrate by a current of $CO_2$, filtering again, and titrating the NaOH, which corresponds to the $Na_2SO_4$ originally present. A number of precautions have to be observed, and corrections to be made; so that the process does not seem to offer any advantage to a direct volumetrical or gravimetrical estimation by $BaCl_2$.

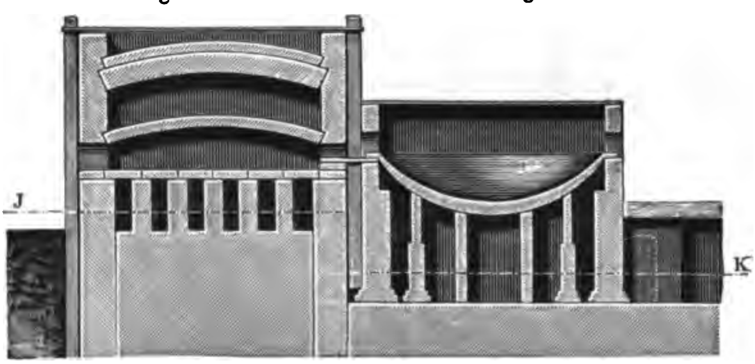
To p. 81. *Construction of the arches of blind roasters (muffle furnaces).*—Cliff (patent No. 1098, March 19, 1879) proposes employing specially moulded hollow lumps of fireclay instead of the double arch generally employed.

To p. 87. *Sulphate-furnaces with two pans.*—Perhaps the most

perfect form of a blind furnace is that observed by the author at Griesheim. The roaster is free at both ends, which greatly facilitates the cleaning of the flues both above and below the muffle. At one long side there are two decomposing-pans, heated by the waste fire of the roaster. The arrangement of flues and dampers is such that the fire of the roaster can be taken, 1st, direct to the main chimney-flue; 2nd, underneath the first pan and then direct to the main flue; 3rd, underneath the first and then the second pan; 4th, underneath the second pan and direct to the main flue; 5th, underneath the second and then the first pan. Thus all possible combinations are practised, and it is always easy to give each pan the precise degree of heat it requires. The pans, although not made of specially good metal, and only 2 inches thick all over, last for nearly two years, till they are fairly worn out by the tools. Each furnace turns out six tons of sulphate per 24 hours.

To p. 93. *Deacon's plus-pressure saltcake-furnace.*—This furnace, briefly described in the text, is intended to avoid the drawback of ordinary muffle furnaces, that whenever their arches &c. are cracked the stronger draught in the fire-flues causes the acid gas to get into the latter and thus to miss the condenser. In Deacon's furnace the muffle is placed at a considerable height above the fire-grate; thus the aspirating action required for feeding the fire with air is

Fig. 129. Fig. 130.




acting already in the space between the grate and the muffle, which is accordingly to some extent playing the part of a chimney. This is supposed to produce an excess of pressure in all the fire-flues, and to cause, in case of leakages, the fire-gas to enter into the muffle,

instead of the muffle-gas coming out. A difference of level of 6 to 8 feet between the grate and the muffle is said to suffice for


Fig. 131.

this. Of course the fire-gas must ultimately be carried away by an ordinary chimney; and it is important that the aspirating action of the latter shall not act too much upon the flues. The arrangement shown in figs. 129 to 135 is said to have succeeded

Fig. 132.

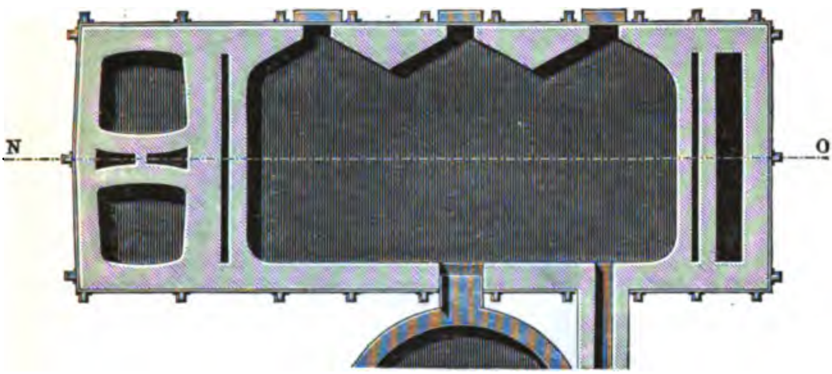
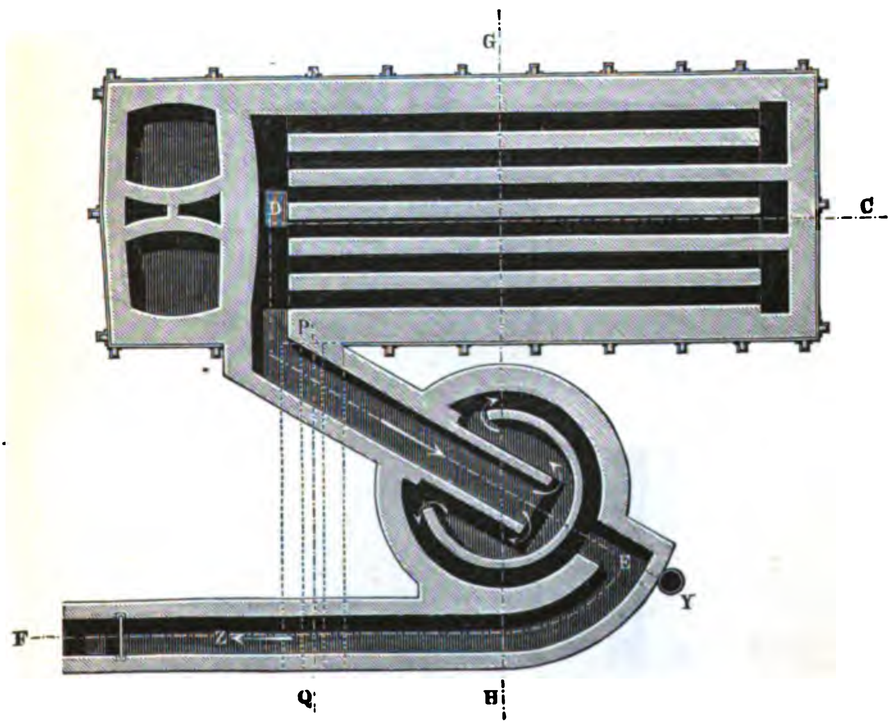



Fig. 133.



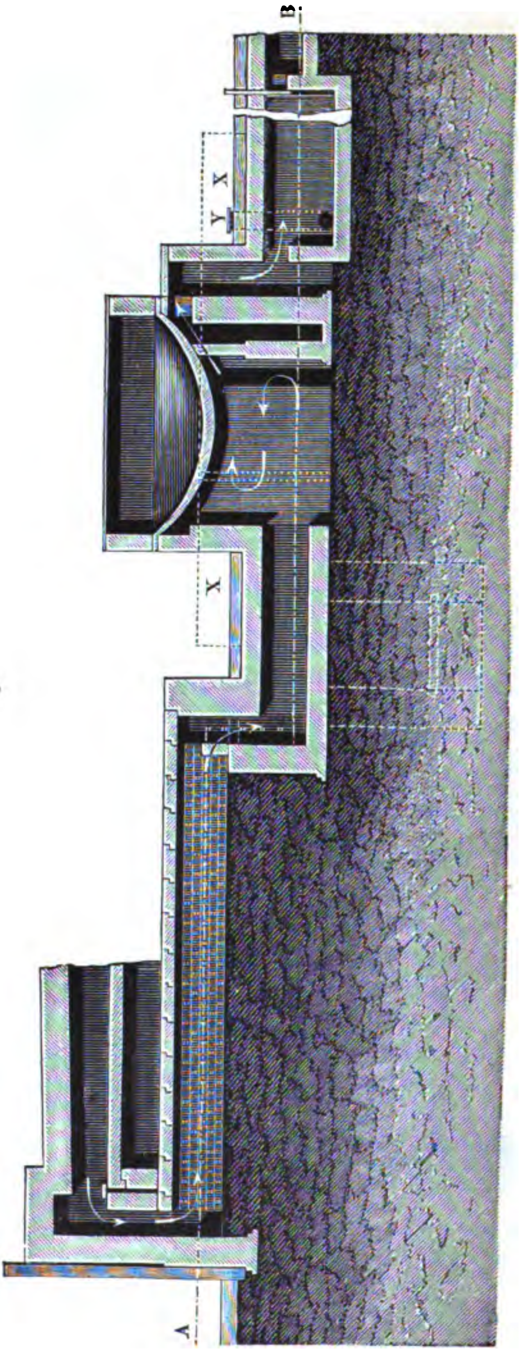



Fig. 134.

very well, to save fuel, and to permit heating the pan by the waste heat of the furnace. This object is attained by forming in the

Fig. 135.


chimney-flue behind the roaster large openings connected with the outer air ("breaks"). The flue ordinarily used is Z; X is a flue serving in exceptional cases when the pan is not to be heated. The breaks are shown at Y and Y′; one of them is between the muffle and the pan, the other behind the pan. An insufficient quantity of air is admitted through the grate, so that the air entering at the "break" between the muffle and the pan still meets with some combustible gases. [The whole is a somewhat rough kind of gas-furnace; a proper generator (gas-producer) would undoubtedly act more completely.]

To p. 107. *A mechanical saltcake-furnace*, similar in principle to Jones and Walsh's, but of different construction in detail, is working very satisfactorily at the Aussig works. It turns out regularly 6 charges of 30 cwt. salt each, or 9 tons in 24 hours, with a pan 11 feet 6 inches wide.

Another furnace has been patented in Germany by Blügel (No. 4207, 1878). Its essential feature is the replacing of metal pans by pans made of brickwork, or of metal lined with brickwork. This is applied both to stationary and mechanical furnaces.

To p. 160. *Hargreaves's process.*—A further patent (No. 2809, July 10, 1880) contains improvements in the mechanical construction of the apparatus, in the arrangement of the heating-flues, and in that of the connecting- and gas-pipes, etc.

To p. 169. *Glauber's salt.*—To obtain good crystals, the solution of sodium sulphate ought in summer to stand at 38° Tw., in winter at 32½° Tw. The solution is allowed to settle overnight and run into coolers, where it is left for two days at least.

To p. 171. *The physical constants of liquid* (condensed) *hydrochloric acid* have been examined by Ansdell (Chem. News, xli. p. 75).

To p. 190. *Condensation of hydrochloric acid.*—The Inspectors' Report for 1877–78, p. 69, states the escape of HCl with chimney-gases, for

| | | | | | | |
|---|---|---|---|---|---|---|
| No. 1 District | (South Lancashire), | at 0·13 | grain | per | cubic foot. |
| „ 2 „ | (Midland) | „ 0·098 | „ | „ | „ |
| „ 3 „ | (Tyne), pan-outlets 0·15, | „ 0·095 | „ | „ | „ |
| „ 4 „ | (Scotland and Ireland) | „ 0·106 | „ | „ | „ |

(It will be remembered that the maximum escape allowed by the Alkali Act, 1874, is 0·2 grain.)

In spite of this favourable result, it cannot be said that trees do grow where none grew before (p. 7). A perfect condensation *can* be attained for close furnaces, as far as the acid passing into the condensers is concerned. There remains a certain loss of acid in the fire-gas, by diffusion through the brickwork, and by accidental leaks. The former loss is very small; the latter is avoided by the "plus-pressure furnace," constructed upon the plan of Gamble, Deacon, and others, in which there is a smaller pressure of gas inside the muffle than outside in the fire-flues (comp. Vol. II. pp. 93, 95, and Vol. III. p. 389). Dr. Smith expects perfect success from the principle applied in the furnace of Cammack and Walker (Vol. II. p. 110); but unfortunately the right mode of carrying it out has as yet escaped detection. According to tests made at Messrs. Gaskell, Deacon, & Co.'s (p. 118 of the Report) the flue-gas of ordinary saltcake-furnaces contained on the average 2·17, but that of the plus-pressure furnaces only 0·54, 0·24, 0·17 grain HCl per cubic foot, the furnace last built showing the best result.

To p. 232. *Construction of condensing-towers.*—The construction shown in fig. 124, in which there is no iron employed for binding the stones, must certainly be most strongly recommended above all others. The author has seen such a tower, for instance, at Griesheim, which has now stood for 30 years, needing no repairs, and is still as good as ever.

To p. 255. *New Systems for condensing Hydrochloric Acid* (Inspectors' Report 1877–78, p. 114 *seq.*).—Fryer adds steam to the gases from the decomposing-apparatus, sufficient to form ordinary muriatic acid when steam and gases are cooled down together. The mixture is passed through glass tubes 1 inch in diameter and 4 feet in length, put into boxes 4 feet square, each box holding 144 tubes. The box is filled with water, which plays round the

tubes and cools the gases sufficiciently to condense most of the HCl, but not all. The remaining work was to be done in "spray-chambers," where revolving disks cause a spray of water in six compartments one above another. This plan was tried at Widnes, but not fully, the spray-chambers never being used at all. None of the tubes was displaced or broken. But there must have been some hitch about it, as the plan was not proceeded with after the first trial. Dr. Smith thinks that it is feasible, and hopes it may be revived. He gives coloured drawings of the apparatus.

Hazlehurst's first apparatus (patent No. 1668, 1877) consists essentially of a hollow cylinder closed at the top and acting as a piston. It rises and falls in a wider vessel, a hydraulic lute being formed at the bottom. On its rising, the acid gases are aspirated into the cylinder; and when it falls they are forced through the liquor at the bottom, which may be water or weak acid. A trial of this apparatus is being made at Widnes.

His latest apparatus* (patent No. 4233, 1879) consists of a Koerting steam-jet, made of Yorkshire flag, by which the gas is drawn through cooling-pipes and then forced (under from 18 inches to 2 feet of water pressure) up two ranges of 12-inch pipes filled with coke and flushed with water. The Yorkshire-flag tower is thus entirely set aside. There is a great advantage in prime cost for one pot and furnace; and the gain is very much increased when the apparatus is applied to two or more. The advantages of this system (which is at work at the Messrs. Mathieson's works at Runcorn) are said to be:—no connexion with the chimney; no expensive foundations; less space occupied; very little ironwork required; no possibility of needing extensive repairs; a saving of half the cost in comparison with condensing-towers, royalty included.

To p. 262. *Testing for escapes of hydrochloric acid.*—In the Hargreaves process some salt is always carried away mechanically by the draught in the moulding and drying apparatus (described Vol. II. p. 133 *seq.*). This would affect the results of the chimney-test for chlorides, unless the salt were kept out. Mr. Fletcher, as stated in the Inspectors' Report 1877–78, p. 76, found that this could be done by filtering the gas through asbestos, which at temperatures above 100° C. does not retain any HCl. Glass wool, on the contrary, retained some acid, probably by its alkaline constituents.

* I owe this description to a private communication from the inventor himself.

The *Committee of Alkali-makers* give the following *rules for the testing of hydrocholric-acid escapes*:—A continuous test over 24 hours in one chimney, with intermittent daily bellows test at nine o'clock, or other specified time, to be taken and recorded; particulars of the work done by the chimney to be given, viz. quantity of fuel-gases passing into it, whether close or open roasters are used, and any other particulars that may be desirable. The observing-apparatus to consist of three bottles or tubes containing not less than 100 c. c. of absorbing liquid, a depth of 3 inches in each. The aperture of the inlet-tube not to exceed $\frac{1}{32}$ of an inch in diameter, and of the second and third $\frac{1}{50}$. Wires for the purpose of measuring this will be supplied by Mr. Muspratt. Absorbing liquid—distilled water free from chloride. Speed of aspiration as near as possible $\frac{1}{4}$ cubic foot per hour. Mode of testing—decinormal nitrate of silver (10·8 Ag. per litre), "chromate indicator." The intermittent test, above alluded to, to be made with bellows at a stated hour, and once daily, but at such time as the escape of hydrochloric acid may be expected to be greatest. Temperature and barometric pressure: the variations of these to be noted, and corrections made to 30 inches bar. and 60° F. The results to be stated in grains per cubic foot.

The above rules do not take into account that the chromate indicator does not act when (as is frequently the case) $SO_2$ occurs in the gas; but we have shown (Vol. II. p. 264) that this can be remedied by oxidizing the $SO_2$ by means of permanganate.

To p. 272. *Conveyance of hydrochloric acid.*—In Germany it is sometimes sent out in very tight casks made of resinous fir. They last a few weeks only; still this mode is cheaper than the employment of glass carboys.

To p. 312. *Soda from sodium chloride and lead acetate.*—Knab and Kuentz (French patent No. 116,530, of Jan. 18, 1877) mix concentrated solutions of these compounds. A precipitate of lead chloride is formed at once, assisted by the action of lime; and alkaline acetate remains in solution. The latter is evaporated, the acetate dried and submitted to dry distillation in a cast-iron retort. Sodium carbonate remains behind. Among the volatile compounds escaping is acetone, for which a use may be found on account of its inflammability. (The yield of acetone is very small, and undoubtedly would not pay for the loss of all the acetic acid; it is, moreover, of no use for any important technical purpose.)

To p. 314. *Soda from sodium chloride and magnesium sulphate.*—A patent of I. Townsend's (No. 1703, 1879) makes a number of proposals in this direction, none of which possesses any essential novelty.

To. p. 323. *Soda from sodium chloride and carbon dioxide.*—At last a process of this kind has been proposed in real earnest. Mr. Carl Funk, of Helmstädt, has thought it worth while to claim the priority over H. Müller (who never thought of proposing the above as a manufacturing process), having in 1866 made the following proposal, which he only now makes public through the Chemiker-Zeitung, 1879, p. 660. Soda is to be made by the action of *liquid* carbon dioxide on common salt, by passing $CO_2$ into a solution of salt, cooled below 0° C., at a pressure of 36 atmospheres. The bicarbonate separated is to be filtered off under the same pressure, and from the solution carbon dioxide and hydrochloric acid distilled off, one after the other. The reader will see that any criticism of this invention is unnecessary. R. Lancaster (pat. 4122, 1879) proposes making soda by passing $CO_2$ into melted NaCl.

To p. 325. *Soda (Caustic) from common salt by the electric current.*—This plan is proposed again by Wastchouk and Glouchoff (German patent 10039, Dec. 2, 1879), with the modification that a contrivance is employed for removing the gases collecting at the electrodes and polarizing them. Both oxygen and hydrogen are conveyed into "gas batteries," which may serve for a new electrolysi

To p. 326. *Soda (Caustic) from sulphate of soda and lime.*—Tessié du Motay, in 1871, took out a French patent on the same lines as Hunter's process. From experiments made in the author's laboratory by Mr. Reisz, it appears that at the ordinary pressure as much as 28·8 per cent. of the sulphate can be decomposed, if the liquid is very dilute (180 parts of water to 1 of sulphate). At a pressure of 5 atmospheres and a proportion of from 25 to 50 water to 1 of sulphate, from 23 to 31 per cent. of the latter were decomposed.

To p. 327. *Soda from sodium sulphate and caustic baryta.*—Dr. Smith (Inspectors' Report, 1877–78, p. 34) believes that caustic baryta can be cheaply made by the process described there—viz., adding a little $MnO_2$ to a solution of BaS and passing a current of air through it. A precipitate of sulphur and a solution of barium hydrate are formed, whilst $MnO_2$ only acts as a carrier of oxygen and remains as before.

His soda-ash process might be formulated thus :—

1. $BaSO_4 + 2C = BaS + 2CO_2$;
2. $BaS + MnO_2 + H_2O = Ba(OH)_2 + MnS + O$;
3. $MnS + 2O = MnO_2 + S$;
4. $Ba(OH)_2 + Na_2SO_4 = 2NaOH + BaSO_4$.

But, unfortunately, the above reaction takes place only in dilute liquids; moreover barium hyposulphite is also always formed; and these circumstances, combined with the expense of reducing the $BaSO_4$ and lixiviating the BaS, would perhaps make the process not economical. But it is certainly worthy of the attention of practical men.

To p. 328. *Soda from barium carbonate and sodium sulphate.*—Dr. O. Schott (private communication) obtained, by melting the above substances at a strong heat, a fused product which yielded with water a strongly alkaline liquor and a residue of almost pure $BaSO_4$. The latter was in a coarsely crystalline state, which explains its not being reconverted on contact with the hot alkaline liquor. But as Schott had to employ an excess of sodium sulphate, his process would be useless from that cause alone; and it would certainly be more expensive than the treatment in the wet way with the aid of carbonic acid. The main difficulty and expense, viz. the recovery of $BaCO_3$ from $BaSO_4$, would still remain to be overcome.

To p. 329. *Soda from sodium sulphate, barium carbonate, and lime.*—V. Wartha (of Pest) has found that this process is easily carried out, even at the ordinary pressure. He left it to the author to continue the investigation in his laboratory, which was done by Mr. Fries. It was found that the decomposition was practically complete if 1½ equivalent of precipitated $BaCO_3$, or if 3 equivalents of native barium carbonate in the finest state of division were employed to 1 equivalent of $Na_2SO_4$ and 1½ of lime. So far the process would be all right; but losing the barium carbonate cannot be thought of, and its recovery from the $BaCO_3$, mixed as it is with CaO, would probably be far too expensive to make the process pay.

To p. 332. *Soda from sulphate, coal, bauxite, and ferric oxide* (patented by Behnke for Germany, No. 7256, April 1, 1879).—The above four materials are ignited together; or else the sulphate and the coal are first heated by themselves. The ferric oxide facili-

tates the decomposition by its affinity for sulphur. The calcined mass is lixiviated; and by treating the solution of sodium aluminate with carbon dioxide, aluminium hydrate and sodium carbonate are obtained. The iron sulphide formed is burned, and the ferric oxide employed over again. This process would probably be attended with most of the drawbacks attached to Kopp's process (Vol. II. p. 341).

To p. 333. *Bauxite.*—The following analyses, by Spence, show the composition of the Irish bauxite formerly generally employed:—

| | Irish Hill. | Co. Antrim. |
|---|---|---|
| $Al_2O_3$ | 48·12 | 43·44 |
| $Fe_2O_3$ | 2·36 | 2·11 |
| $SiO_2$ | 7·95 | 15·05 |
| $H_2O$ | 40·33 | 35·70 |
| | 98·76 | 96·30 |

The second quality especially is of little use, owing to the large proportion of silica it contains.

Very much superior is the mineral discovered a few years ago (before the Irish-Hill bauxite) by Mr. J. F. W. Hodges, of Belfast, at Glenravel, co. Antrim, which is now of primary importance. His analysis (with which that of Mr. Spence closely agrees) shows

61·89 $Al_2O_3$, 1·96 $Fe_2O_3$, 6·01 $SiO_2$, 2·32 $TiO_2$, 27·82 $H_2O$.

To p. 339. *Soda from sodium sulphate, lime, and sulphur* (Gutzkow's process).—This process is accurately described by the inventor in 'Dingler's Journal,' ccxxxvi. p. 148. He claims for it practical usefulness under circumstances such as exist in California, where the crude sulphate of soda from the manufacture of nitric acid (nitre cake) has next to no value, where sulphur (Japanese brimstone) costs only twice as much as English coal, and calcium sulphate is in great request by paper-makers and builders. A solution of $Na_2SO_4$, mixed with lime and treated with an excess of $SO_2$, is decomposed up to 90 per cent.; the solution contains principally sodium bisulphite, with calcium bisulphite and sulphate. This solution is causticized by lime without heating, but, even in very dilute solutions, very imperfectly so; with 30 grains to the litre 75 per cent. of sodium sulphite remain unchanged. The

residual (impure) calcium sulphate is employed as "pearl hardening" (Vol. II. p. 576), but does not seem to have found much favour as such, according to the inventor's own account. The caustic liquor is boiled down and salted out as usual; the salts contain a good deal of sodium sulphite along with sulphate and caustic. The inventor claims to use only 4 tons of coal to the ton of caustic; but, considering the dilution of his liquors, this does not seem credible; and it has never been proved by experience, as the process was never carried out on a large scale.

To p. 357. *Reducing alkaline sulphates by means of sulphuretted hydrogen.*—This process is patented by E. G. Bong (No. 845, March 6, 1879). The $H_2S$ is obtained by decomposing by means of $CO_2$ the sulphides formed, and is supplemented by generator-gas. From this $CO_2$ is formed, which converts a portion or, in case of excess and in the presence of steam, the whole of the sulphide into carbonate.

To p. 359. *Soda from sodium nitrate and calcium carbonate.*—Experiments made in the author's laboratory by Mr. Schäppi prove that the decomposition is practically complete if to 1 equivalent of $NaNO_3$ 2¼ of $CaCO_3$ are employed. Platinum was strongly acted upon by the ignited mass. Of the nitric acid 93 per cent. could be recovered on the small scale.

To p. 362. *Quality of the sulphate for black-ash.*—When, as is now usual on the Continent, the very highest strength of ash, up to *real* 57 per cent. $Na_2O$, is aimed at, the sulphate must, of course, be as free as possible from common salt. The maximum it should contain is 0·5 per cent. NaCl as shown by the analysis of the tank-liquors. Some manufacturers state that the purer the sulphate from NaCl the less tendency there is in the tanks for $Na_2S$ and $Na_2SO_4$ to be formed, apart from that originally present; but accurate data on this point are still wanting.

To p. 416. *Firing of revolving ball-furnaces.*—A medium between the ordinary and the gas furnace is that of Pauli (pat. 3825, 1879). He introduces into the fireplace only enough air to form a combustible gas (carbon monoxide), and allows the air for completing the combustion to $CO_2$ to enter at the "eye," where in the ordinary furnace very much superfluous air enters, cooling the furnace and carrying away much heat. Pauli's process is intended to avoid this, and thus to save fuel.

To p. 426. *Removal of cyanides from black-ash liquors.*—Carey,

Gaskell, and Hurter (patent No. 2939, 1879) propose treating the liquors with air or with sulphur, polysulphides, or hyposulphites, the latter in order to convert the cyanogen compound into sulphocyanide, which is harmless. The liquor ought to be heated to 150° C., which can be done by forcing it continuously through coils of pipes heated from the outside. The reactions taking place are represented as follows :—

(1) $5Na_2S_2O_3 + Na_4FeCy_6 = 6NaCyS + 2Na_2SO_3 + 2Na_2SO_4 + FeO$;
(2) $6Na_2S_5 + 4Na_4FeCy_6 = 24NaCyS + 2Na_2S + 4FeS$.

To p. 479. *Testing tank-waste.*—At some works the mistake is made of *drying* the tank-waste before testing, in which case there is always some calcium sulphate formed, which on treatment with water decomposes with sodium carbonate, so that less soluble alkali is found in testing than the waste really contained. To prevent this mistake, the waste should be tested quite fresh and undried. If desired, the moisture can be estimated in a separate sample; but for practical purposes it is sufficient to assume it =33 per cent.

To p. 480. *Lixiviation of black ash.* The process described here as best for the lixiviation of revolver-ash, viz. beginning with cold water and raising the temperature of the strong tank by injecting a little steam (preferably into the overflow from the preceding tank) is employed at many works for hand-made ash as well, and with the best results. It is quite possible to operate in such a way that the sulphide and sulphate in the liquor do not exceed that found by testing the black ash in the laboratory, and thus, with very good sulphate and faultless balls, to turn out all the soda ash at 57 per cent. real (not "Liverpool") strength, as the best German and a few English works do. But for this purpose it is necessary not to exceed 50° C. even in the strong tank; and at this comparatively low temperature it is only when the balls are as porous as possible that they can be completely washed. The secret of this seems to be, forming as much caustic lime as possible in the ball-furnace, which can only be attained by working it as *hot* as possible. The caustic lime, by slaking as the black ash is brought into contact with water, swells up and causes the dense mass to be thoroughly loosened. It would appear that this cannot be done to a sufficient extent by a *mechanical* mixture of lime, *i. e.* Mactear's process (p. 419), but only by applying enough

heat to causticize a sufficient quantity of the excess of calcium carbonate intimately mixed with the sodium carbonate in finished black ash. Although black ash made in this way contains more caustic lime than that made at a lower heat, yet the liquor obtained from it contains less caustic soda, because, on account of the much looser state of the black ash, the lixiviation takes place more quickly and at a lower temperature. The caustic soda in itself is not a very serious evil, as it can be completely removed by proper carbonating; but along with an excess of it, owing to the higher temperature and longer duration of lixiviation, a good deal of sodium sulphide is also formed, thus seriously deteriorating the quality of the soda ash.

To p. 502. *Mechanical fishing- and drying-pan.*—Thelen's pan, described and figured in the text, has been slightly modified in a few details since. It is used at several German works with the greatest success, going quite automatically for many (at least upwards of six) months day and night without any need of cleaning out. Of course the liquors ought to be very well settled; and it is also very preferable to carbonate them first. At Griesheim all the salt supplied by the pan contains 98 per cent. $Na_2CO_3$. An additional patent (Germ. patent No. 7681, 1879) describes a modification of Thelen's pan, adapted for drying (finishing) and grinding the carbonate. By the most recent combinations of Thelen's apparatus it is stated that each pan turns out 10 tons of finished soda-ash per day, with a consumption of 90 to 112 lb. of coal per ton, and at a cost for labour of 10*d.* per ton for boiling down, drying, and packing, all together representing a saving of 3*s.* 5*d.* per ton at the Rhenania works at Aachen, where the invention was made. The author has received very good accounts of it from other works as well.

To p. 520. *Carbonating the soda liquors and finishing the ash.*—Important progress has lately been made in this respect, as will be seen from a description of the process as now carried on at Griesheim from the author's own observation. The liquor is first thoroughly settled on the continuous plan, by running it through a number of large tanks, each continually overflowing at the opposite end into the next. The perfectly clear liquor is run down an iron column filled with coke. Into this enters the gas from a boiling-down pan for soda-crystal mother-liquor, heated from the top. This gaseous mixture of $CO_2$, O, N, etc. is consequently

always saturated with moisture; so that the liquor is *not* concentrated in the carbonating-tower. This is of importance, as it has been found that liquors above 50° Twadd. are not easily carbonated through. The gas is aspirated by a small air-pump, and forced into the tower at the top, escaping at the bottom into a flue leading into the chimney. If the gas enters at the bottom, crusts are formed very quickly, which partially stop up the interstices between the pieces of coke. If the plan just described be employed, the coke can go for several months before it need be taken out. This pumping of gas through a coke-tower takes very much less power than the Ludwigshafen process (p. 519), where the $CO_2$ is forced through a column of liquor.

The end of the process is learned by testing the liquor with turmeric-paper. This turns yellowish red so long as even a trace of caustic remains in the liquor, but much more deeply brownish red when there is no more caustic present. To make sure, the colour of the paper is always compared with that of another paper dipped into a strong solution of pure sodium carbonate; only when the two are quite equal in colour is the process stopped and the liquor (which now contains a little bicarbonate) run away.

Although the carbonating takes place with thoroughly settled tank-liquor, it is found that after carbonation the liquor, on being heated, deposits a good deal more of impurities. The carbonated liquor therefore, before entering the Thelen fishing-pan (compare addendum to Vol. II. p. 502), is run through three or four tanks in succession, in which it is gradually heated up to 80° C., as the waste heat of the pan-fire (which itself is only the waste fire of a black-ash furnace) passes underneath them; and on its way again a good deal of deposit is formed, which of course must not be disturbed until it is time to remove it from the tanks.

The salt formed in the mechanical fishing-pans (which in this instance cannot possibly be called "black salt") is almost pure monohydrated sodium corbonate; it is constantly taken out by the scrapers, and carried over the side of the pan, along with a little mother liquor. Even the latter, owing to the careful work, is so pure that it is either made into caustic soda of high strength *without any salting out*, or into soda crystals, the last mother liquor of which still yields soda ash of 90 per cent. $Na_2CO_3$. The drained salt itself might be dried in any ordinary calcining furnace or in the new Thelen pan (p. 402) without any trouble, as it is quite free

from caustic and sulphides; it yields regularly soda ash of 98 per cent. $Na_2CO_3$. But at Griesheim another mode of drying is preferred, with the object of both economizing fuel and obtaining perfectly white soda ash without having to destroy the cyanogen compounds. (It is objected there to the Pechiney process, Vol. II. p. 421, that it is too difficult to avoid leaving a little sulphate in the ash.) The salt is dried, at a heat not exceeding 150° C., in cast-iron exactly similar in size and shape to gas-retorts. Each retort yields 4 cwt. of ash. They are set in rows and heated by a portion of the waste heat from the black-ash furnace, which has also done the boiling-down; so that both the boiling-down and finishing of the ash require no fuel whatever for themselves. Care must be taken that the heat does not exceed 150° C., at which point the sodium ferrocyanide is not yet decomposed, and therefore the ash is not discoloured at all. If any of the retorts is allowed to get too hot, the salt begins to colour at once; but this is easily avoided, as the fire-gases have been previously cooled down so much underneath the boiling-down pans. This plan requires also much less manual labour than the ordinary plan of boiling-down and finishing. [But the retorts seem inferior to the new Thelen pan (p. 402), which requires still less labour, and where the heat of drying can be regulated with greater certainty.]

Exactly the same plan (Thelen's pans with heated settlers and drying-retorts) is applied to a Daglish's revolving furnace which was in course of erection at Griesheim during the author's visit there.

To p. 522. *Desulphurizing tank-liquor by Pauli's process.*—The following is a more accurate description of the same. To the tank-liquor is added a dilute solution of some manganese salt, in the proportion of 1 gram $MnCl_2$ to each litre of the liquor. Then a strong current of air is blown through the liquor, heated up to 50° or 60° C. The precipitated MnO takes up oxygen from the air and is raised to a higher degree of oxidation; but this, at the moment of being formed, gives up its oxygen to the sulphides in the liquor. The white precipitate of MnO thus remains unchanged as long as any sulphides are present, but afterwards turns brown and at last black. Now the blast is stopped, the liquor allowed to settle, and the clear portion drawn off. The operation lasts from three to eight hours, according to the power of the blast and the percentage of sulphides. The brown or black mud remaining behind is

employed for desulphurizing fresh tank-liquor; and thus the same small quantity of manganese oxide is used over and over again, till it is too much contaminated by impurities, when it is removed. This process has been very successfully carried out both in German and English factories.

A patent of Weldon's (No. 339, of Jan. 28, 1879) is very similar to Pauli's, but omits the regeneration of the manganese oxides in the liquid itself, instead of which the MnS formed is to be dissolved in hydrochloric acid, and the $MnCl_2$ worked up along with that from the Weldon chlorine-process.

*Desulphurization of soda liquors by means of hydrated zinc oxide.*—This plan was laid down by Scheurer-Kestner in a sealed note dated Jan. 27, 1869, deposited with the Société industrielle de Mulhouse. The note was opened on Jan. 14, 1880; and it was stated that the process had been working well from the first. There must be no more zinc oxide added than just what is necessary for removing the sulphur, to be ascertained by frequent testing: an excess of the oxide would be dissolved in the soda liquor. The precipitated zinc sulphide is separated by filtration, and decomposed by hydrochloric acid; the $H_2S$ is absorbed in purifiers like those of gas-works, and the solution of $ZnCl_2$ employed for recovering the $Zn(OH)_2$ by precipitation with lime. (Bull. Soc. Mulhouse, 1880, p. 30.)

To p. 550. *Composition of soda ash.*—The following analysis of *ordinary* German soda ash, made by the Leblanc process, as supplied in 1879 to the ultramarine-works of R. Hoffmann (communicated by him in the 'Chemische Industrie,' 1879, p. 418), will, if contrasted with the analyses tabulated in the text, give a good idea of the progress made since that time:—

| | |
|---|---|
| Sodium carbonate | 98·20 |
| „ chloride | 0·10 |
| „ sulphate | 0·69 |
| „ sulphite and hyposulphite | 0·10 |
| Insoluble | 0·11 |
| Moisture | 0·67 |
| | 99·87 |

Jurisch, in 'Chem. Industrie,' 1880, p. 241, gives a number of analyses of black ash, revolver-soda, red liquors, Pechiney liquors, etc. from a Lancashire works.

To p. 554. *A new cask-packing machine* by Büssing, of Brunswick, is described in the 'Chemische Industrie,' 1879, p. 443.

To p. 560. *Purification of liquor for crystal soda.*—The caustic soda, which is so troublesome in making soda crystals, can be instantly and completely removed by adding during the dissolving either a little sodium bicarbonate or, more cheaply, ground magnesium carbonate (natural magnesite). This is the secret of some continental crystal-makers.

To p. 595. *Causticizing of soda liquors.*—According to Solvay's patent of 1879, lime, if slaked in a solution of calcium chloride or ammonium chloride, yields a granular hydrate which causticizes soda liquors most readily. It is sufficient to run the liquor, suitably diluted and heated, over a layer of the granular hydrate, which does not lose its form and is much more readily washed than the ordinary lime mud.

To p. 597. *Parnell's plan for causticizing soda liquor under pressure,* mentioned in the text, seems to be successful and to effect a considerable saving of fuel. The operation takes place in horizontal cylinders, like steam-boilers, about 7 feet in diameter, and 30 feet long, provided with an agitating-shaft and "cages" for the lime. Each charge consists of about 400 cubic feet of soda liquor, and takes from 3½ to 4 hours, at a steam pressure of from 45 to 60 lb. to the superficial inch. 90 or 92 per cent. of the soda are causticized; the caustic liquor comes out up to 32° Twaddle strong. The mud contains from 3 to 4 per cent. of free lime. Each ton of 70-per-cent. caustic requires 15 or 16 cwt. of lime. One apparatus turns out about 70 tons weekly.

Causticizing soda liquors without heat, *by pressure only,* was proposed simultaneously by Wells (pat. 3803, 1879) and Menzies (pat. 3804, 1879).

To p. 604. *Caustic soda.*—It is mentioned in the text that the German caustic-makers can do without boat pans, as they have much purer liquors than are usual in England. The author can confirm this from recent observations. At some German works the liquors are first carbonated, so as to free them from iron and alumina; but this cannot be done completely, as some more is deposited when the carbonated liquor is heated (comp. p. 403). Even without that plan some German alkali-makers entirely dispense with salting out and settling, and yet, by boiling down the liquor straight from the causticizing-tanks (of course well filtered), they make all their

caustic 71 or 72 degrees *real* (not "Lancashire test") soda, or at least 70 per cent. $Na_2O$ as NaOH, without reckoning the carbonate (which is not accepted as counting for degrees by the German consumers of caustic soda).

To p. 616. *Formation of graphite in finishing caustic soda.*—According to Thalheim ('Chemische Industrie,' 1880, p. 52) the graphite cannot be due to the composition of ferrocyanides, since it is observed even when the liquor is quite free from cyanogen compounds, but it comes from the metal of the pots.

*Unoxidized sulphur in caustic.*—At Griesheim it is found that when this comes down to 0·05 per cent. of $Na_2O$, the mass does not settle well and turns greenish or bluish. It is usually kept at 0·13 of sulphur per cent. of $Na_2O$.

*Oxidizing the fused caustic by air* is stated by some to be more destructive to the pots than by nitre. Opinions seem to be divided on this point. At Griesheim (where nitre is employed) there are pots which have turned out more than 1000 tons of caustic.

To p. 620. *Packing the caustic into drums.*—At Griesheim this is done in a very expeditious and cleanly manner by means of a tramway running parallel with the caustic-pots, at a short distance from them. The tramway is sunk so that the small bogies running upon it are level with the ground. The drums, standing upon the bogies, are run underneath the shoot one after another, the shoot being a little raised at the lower end when the drum is full, and lowered again when the next drum has taken its place. Otherwise the shoot always remains in the same place from the beginning to the end.

*Grinding caustic.*—Menzies (patent No. 4274, 1879) grinds the caustic whilst quite hot, in a mill provided with a grated bottom.

To p. 646. *Pentathionic acid.*—Spring maintains his position as to the non-existence of this acid (Annal. d. Chemie, vol. cci. p. 377); but an independent research by Takamatsu and Watson Smith (Chem. Soc. Journ. 1880, p. 592) confirms the existence of pentathionic acid.

To p. 689. *Recovery of sulphur from tank-waste.*—Pechiney (patent No. 3194, Aug. 8, 1879) tries to limit the oxidation of the "yellow liquors" by means of a current of air (preferably aided by steam) so that no more $H_2S$ shall be given off by acids, and yet no $SO_2$ be formed. During this operation about $\frac{1}{4}$ of the CaO is precipitated as hydrate and removed by decantation.

The liquor is now to contain only calcium thiosulphate and and polysulphide (?) (thus,

$$4CaS_2+4O=CaO+CaS_2O_3+2CaS_3),$$

and is decomposed by the exact equivalent of sulphuric or hydrochloric acid, by which all the sulphur is precipitated, thus,

$$CaS_2O_3+2CaS_3+6HCl=3CaCl_2+3H_2O+8S.$$

[It seems very doubtful that the oxidation can be directed precisely in the way desired.]

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## ADDENDA TO VOL. III.

To p. 37. *Ammonia ash.*—According to reliable information, the apparatus constructed by Wegelin and Hübner upon the system of Polacsek has been a failure; but that of Boulouvard is working well in the south of France, at Sorgues.

To p. 43. Unger's apparatus is described in detail in Wagner's 'Jahresbericht,' 1879, p. 299. An additional patent of his (German patent 10392, Dec. 21, 1879) contains some improvements on his first apparatus.

To p. 51. *Manufacture of ammonia.*—W. Müller and E. Geisenberger (patent No. 1481, 1879) propose to make ammonia by decomposing barium or potassium nitrate or nitrite by heat and passing the gaseous products along with steam, into a red-hot retort filled with coal. The bases are reconverted into nitrates or nitrites by bringing them into contact with nitrogen and oxygen under the influence of electricity. In another patent (No. 1592 1879) they simplify matters by making ammonia directly from nitrogen and hydrogen by means of electricity. Their proposals are singularly unpractical. The process of Rickman and Thomson, briefly mentioned in the text, is stated to yield very favourable results, on the authority of the inventors. What that is worth, time will show.

Basset (patent No. 4338, 1879) utilizes for the manufacture of ammonia the property of boron to combine with nitrogen.

To p. 165. *A mechanical apparatus for making bleaching-powder* on a new principle has been invented by Kopfer (German patent 9398, 1879). The chlorine is introduced halfway above the bottom of an octagonal chamber, 13 feet high, into which sifted

hydrate of lime is introduced from above, either continuously or periodically, in the form of a fine spray. This is produced by means of a revolving drum with perforated jacket, which is fed with calcium hydrate from above by a hopper. The bleach may accumulate in this way up to a height of 5 feet without interrupting the work; and the loss of chlorine and nuisance on opening the chamber may be entirely avoided by absorbing the residual chlorine gas by means of calcium hydrate, introduced as above, in a quantity calculated from an analysis of the chamber-gases. (It is not very probable that this apparatus will be more successful than the other mechanical contrivances for making bleach hitherto proposed; the difficulty of making such an apparatus to withstand the action of chlorine gas would be very great indeed.)

To p. 307. *Boiling down chlorate-of-potash liquor.*—Contrary to what is stated in the text, lead pans seem to answer very well, if heated by a coil of steam-pipes, quite similar to Curtius's pan (Vol. I. p. 503). Iron pans are *not* to be recommended, because the hot chlorate solution acts upon the iron so that much chlorate is destroyed and much mud of iron oxides is formed. For the same reason, at the continental works, lead coolers are preferred for the first crystallization as well.

To p. 311. *Utilizing the mother liquors from chlorate of potash.*—The reason why it is so difficult to employ these for making chlorine is that the evolution does not take place at a low temperature, and at a higher temperature is too violent to be under control.

To p. 318. *The employment of Deacon's chlorine process in the manufacture of chlorate of potash* is carried out with perfect success at a Berlin factory, where, however, not a single one of Deacon's apparatus is used, all of which, as stated by the owner of the works to the author, have turned out to be useless for his purpose. The "finishing" of the chlorate liquor in the absorbers by the dilute gas of the above process presented at first great difficulties; but at Berlin these have been completely overcome.

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VOL. I. p. 26. See ERRATUM, *infrà*, p. 410.

## ERRATUM IN VOL. I.

The formula $\frac{144\cdot38}{144\cdot38-t}$ for reducing specific gravities, taken at a temperature $t$, to 0°, as given on p. 26, Vol. I., is *wrong*, as Mr. Watson Smith has pointed out to the Author, who had taken it from Gmelin-Kraut's 'Handbuch der Chemie,' vol. i. part 2, p. 208, into which it must have crept by some mistake. The table of differences, given in the same page for the same purpose, is *right*.

# ALPHABETICAL INDEX.

B.



C.

R.



S.

T.



U.



V.



W.

THE END.

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